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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 1 April 1959, the Chair being taken by D. L. Samuel, a member of Council.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman introduced the authors, and the following paper was presented in summary:

HYPOID GEAR LUBRICANTS AND ADDITIVES *

By J. S. ELLIOTT, † N. E. F. HITCHCOCK † (Member), and E. D. EDWARDS †

SUMMARY

A brief history is given of the development of hypoid gear oils and the methods used for their evaluation in Great Britain and in the U.S.A.

For some years small laboratory extreme pressure testing machines have been regarded with disfavour and reliance has been almost solely on full-scale axle tests. Some evidence, however, has now been obtained which points to the possibility of using laboratory EP testing machines to achieve correlation with high-speed and low-speed high-torque axle tests.

Work has been done using labelled sulphur and phosphorus compounds in an attempt to throw light on the mechanism of action of EP additives.

INTRODUCTION

SINCE the inception of the hypoid gear in the U.S.A. in 1925 its popularity has steadily increased, particularly in the post-war years, and it has now been adopted by the majority of motor manufacturers both in the U.K. and in the U.S.A. for passenger cars and in many instances for heavy lorries also.

The advantages of the hypoid gear over the spiral bevel and the basic requirements of a satisfactory lubricant have been discussed by Towle,[1] who has also reviewed the development of specifications and test procedures for these lubricants up to 1955.[1,2]

The high loads and sliding speeds implicitly involved in the operation of the hypoid gear have from the outset necessitated the use of the so-called "extreme pressure" (EP) additives, without which scuffing of the gears occurred. This took place even when using mineral oils admixed with fatty oils or polar additives designed to reduce the coefficient of friction. These EP additives originally consisted of elementary sulphur or sulphurized fatty oils, sometimes with chlorine compounds and/or lead soaps.

While these additives generally satisfactorily performed their designed function of preventing scuffing of the gears under high-speed high-load conditions, they failed to overcome a totally different type of gear failure which sometimes occurred under low-speed high-torque operating conditions, *e.g.* in heavily loaded lorries driving in hilly districts. Failure of the gears in such circumstances is not due to scuffing but to rippling, ridging, or other forms of surface distress. Corrosion due to the partial decomposition of the EP additives in the presence of moisture was another problem, while in some cases the use of chemically active sulphur compounds led to the corrosion of cuprous metals present in the system.

These problems were to a large extent overcome by the use of composite additives containing chlorine, sulphur, and phosphorus in balanced proportions and with controlled degrees of chemical activity. Additives of this kind have been in use for the past thirteen years in the MIL-L-2105 type hypoid gear oils which have been widely used both in the U.K. and the U.S.A. in both passenger cars and lorries, following the run-in period.

For factory fills, however, it has often been necessary to use different lubricants giving greater resistance to scuffing. These have contained additives either of the lead soap–active sulphur type or sulphur–chlorine type having greater chemical activity than the MIL-L-2105 additives.

Clearly a universal hypoid gear oil suitable for both factory fills and general use in both passenger cars and lorries would be the ideal lubricant, and work has been in progress for several years, particularly in the U.S.A., with this objective in view. Meanwhile, gradually increasing demands on the lubricant made by greater loads, higher sliding speeds, and higher operating temperatures have exposed the limitations of the MIL-L-2105 oils and given impetus to the development of new and more severe approval test procedures and of new additives to cope with the situation.

The development of composite multi-functional

* MS received 19 February 1959.

† C. C. Wakefield & Co. Ltd.

additives capable of providing adequate protection of the gears against scuffing under conditions of high-speed operation and shock loading and at the same time preventing surface distress under low-speed high-torque conditions has been complicated by the fact that additives of quite different types are required to cope with the two different situations. Furthermore, these additives often exhibit "incompatibility" in the sense that they interfere with one another's normal function. This phenomenon has been mentioned by Blok [3] and Smalheer and Mastin,[4] the latter having put forward a tentative partial explanation in the discussion on their paper, although obscurity still surrounds the whole subject.

Another hindrance to the development of new multifunctional EP additives has been the reliance almost exclusively for years past on full-scale axle tests for evaluating hypoid gear oils, small laboratory EP testing machines having been regarded as unreliable and incapable of yielding useful information about the performance of such oils in service.[1,2,5,6]

It would seem that some of the statements made about these small machines have been too sweeping, or perhaps the machines have not been used with sufficient discrimination, bearing in mind the particular property of the lubricant to be evaluated.

In this paper a brief account is given of work which the authors have carried out using the four-ball, SAE, and Almen machines, which, though by no means complete, points to the possibility of these machines being used to predict the behaviour of hypoid gear oils in the full-scale axle tests.

Some work has also been done with a view to elucidating the mechanism of action of typical components of hypoid gear oil additives and, while again this work is only in its early stages, it does appear already to have yielded useful information bearing on the reason for the "incompatibility" of different types of additives.

Before describing the experimental work, however, it is necessary to discuss briefly the evolution of the hypoid gear oil and methods for evaluating its performance in Great Britain and in the U.S.A.

DEVELOPMENTS IN THE U.S.A.

For many years no general specification existed covering lubricants for hypoid rear axles, individual manufacturers often issuing their own specifications written around oils they themselves had tested and found to be satisfactory.

In 1942 a Federal Specification, designated FS-VVL-761, was issued which was later renamed U.S. Army Specification 2-105A. Oils qualified under this specification were required to contain sulphur and chlorine, and the qualification procedure included a shock test on a Chevrolet car, a high-torque test on a Chevrolet axle, and tests on the SAE machine.

In 1946, largely as the result of experience gained during the war, U.S. Army Specification 2-105 B was introduced, this being subsequently renamed MIL-L-2105. This specification called for additives having improved anti-corrosive properties towards cuprous and ferrous metals and superior lubricating properties under low-speed high-torque conditions. These properties were achieved at the expense of a certain reduction in load-carrying ability under high-speed conditions. The shock test and SAE machine test were accordingly eliminated from this specification, the three principal qualification tests being a high-speed low-torque test on a Chevrolet car (CRC-L-19), a low-speed high-torque test on a Chrysler $\frac{3}{4}$-ton truck axle (CRC-L-20), and a moisture corrosion test on a Chevrolet car axle (CRC-L-21), details of the test procedures having been fully described by Towle.[1] The L-20 test was also used to evaluate the sludging propensities and corrosion tendencies of the oil, the laboratory stability tests in FS-VVL-761 specification being thereby rendered redundant. It should be pointed out that the L-20 test differed from the high-torque test in the earlier specification in that in the latter test scoring was the criterion of failure, whereas extensive tests carried out in the U.S.A. proved that scoring never occurred under low-speed high-torque conditions of operation, even when these were so severe as to exceed the mechanical strength of certain axle members.[6] In the L-20 test failure, when it occurred, was due to deformation normally by ridging or rippling or both.

In the past few years interest in this field has been intensified in the U.S.A. The aim has been improvement of hypoid gear oils in various ways, namely:

1. Anti-scoring properties under high-speed conditions.
2. Performance under low-speed high-torque conditions.
3. Stability and corrosion over a higher temperature range.

This work has culminated in the appearance early in 1959 of a new U.S. specification for a multi-purpose gear lubricant designated MIL-L-002105A (Ord.) (dated 8 Dec. 1958), issued as a limited co-ordination specification which can be "used in lieu of" MIL-L-2105 by all services. Some of the work leading up to the formulation of this specification has been described in a CRC Report [7] and by Sands,[8] Heinen,[9] and Raymond.[10]

In this specification the L-19 and L-20 tests have been replaced by more severe tests designated L-42 and L-37 respectively, comparative test details being summarized in Tables I and II.

The L-42 test differs from the L-19 test in that the peak torques are approximately 2–3 times the L-19

levels. In the L-37 test the load is about 30 per cent higher than in the L-20 test and the maximum oil temperature is 275° F instead of 250° F. There is also

TABLE I

Comparison of L-20 and L-37 Low-Speed High-Torque Axle Tests

	L-20	L-37
Axle	Chrysler ¾-ton army truck	As L-20
Gear ratio	5·83 : 1	As L-20
No. of runs per test	1	2
Gear treatment	None	One phosphated, one uncoated
Break-in conditions:		
Ring gear speed	62 rev/min	None
Ring gear load	6000 inch lb	
Temperature	140° F	
Time	20 minutes	
High-speed conditions:		
Ring gear speed	None	440 ± 5 rev/min
Ring gear load		9460 ± 150 inch lb
Temperature		300° F max.
Time		100 minutes
High-torque conditions:		
Ring gear speed	62 rev/min	80 ± 1 rev/min
Ring gear load	32,311 inch lb	41,800 ± 150 inch lb
Temperature	200°–250° F (cycling)	275° ± 3° F
Time	30 hours	24 hours

TABLE II

Comparison of L-19 and L-42 High-Speed Axle Tests

L-19 Test	
Axle	Chevrolet (9/37 ratio) installed in a Chevrolet car or mounted on a chassis dynamometer.
Procedure	1. Run in for 5–25 miles at 25 m.p.h. max. 2. Accelerate to 40 m.p.h., close throttle, and coast to 10 m.p.h. with clutch engaged (Repeat 4 times). 3. Accelerate gradually to 60 m.p.h., then rapidly to 80 m.p.h., and coast to 60 m.p.h. with clutch engaged (Repeat 10 times).
L-42 Test	
Axle	Spicer Model 44–1 (47 : 12 gear ratio)
Procedure	1. Run in at 600 rev/min wheel speed and 40 ft lb load for 10 minutes, followed by cycling between 600 and 400 rev/min 4 times (oil temp 225° F). 2. Further run in at 850 rev/min and 52 ft lb for 20 minutes, followed by cycling between 850 and 700 rev/min 4 times (oil temp 225° F). 3. High-speed test cycling between 550 and 1100 rev/min (5 cycles) under inertia loading only (oil temp not controlled —normally above 280° F). 4. Shock test at 550–650 rev/min (cycled 10 times) and 131 ft lb (oil temp 280° F at start).

a preliminary high-speed test prior to the high-torque test.

The new specification also calls for a moisture corrosion test and a thermal-oxidation stability test in addition to the usual physical tests and a copper strip corrosion test (3 hours at 250° F).

Alongside the development of the new test procedures, new multi-functional chemical additives have been produced by the additive manufacturers, these being capable of being used at different concentrations to provide satisfactory performance at MIL-L-2105 and MIL-L-002105A levels. At still higher concentrations these additives will enable oils to pass tests more severe than the L-42, such as the Buick 10A shock test. In the development of the L-42 test a series of reference oils containing one of these additives in different proportions was used in a co-operative research programme,[7,8,10] and reference will be made to these again in the experimental part of the paper.

DEVELOPMENTS IN THE U.K.

In the U.K., hypoid gear oil development has to some extent followed the trend in the U.S.A. Thus the British Ministry of Supply issued in 1945 CS.2091 specification covering hypoid gear oils in the SAE 80 and 90 viscosity classes and containing additives inspected and approved by the U.S. Navy Department. The additives concerned were approved to FS-VVL-761 specification, and the oils were merely required to pass copper strip corrosion (no blackening at 212° F, blackening at 300° F—1 hour), steel corrosion, and stability (300° F) tests, in addition to the usual physical tests.

Subsequently CS.2091 was amended to relate to approved 2-105 B additives, the copper strip corrosion test being accordingly modified (no blackening at 250° F—1 hour). Several minor modifications of the specification were made, the last, CS.2091 F, appearing in Nov. 1952.

In 1954 a new specification, CS.2758, was issued, this specification including high-speed and high-torque axle tests for the qualification of additives, using a Standard Vanguard axle as well as copper and steel corrosion tests and a storage stability test.[2]

More recently the Vanguard axle tests have been abandoned due to lack of repeatability and insufficient ability to discriminate between oils regarded as satisfactory or unsatisfactory in field performance. CS.2758 has now therefore been superseded by CS.3000 (dated 17 Dec. 1957), which is rather similar to the old CS.2091F, additives being approved on the basis of satisfactory past experience and the old laboratory corrosion and stability tests being carried out together with one additional steel strip corrosion test.

For general usage in passenger cars and trucks, MIL-L-2105 type oils have been used in the U.K. for at least ten years with generally satisfactory results. Some manufacturers recommend this type of oil for factory fills, whereas others demand an oil of greater load-carrying capacity under high-speed conditions. One such oil, which may be considered generally to be of the FS-VVL-761 type with an additional anti-corrosion/anti-wear additive, has been and still is giving very satisfactory service. In general, the need for oils of MIL-L-002105A performance level does not appear to be felt in Britain as yet, nor is there the same concern about rippling under low-speed high-torque operating conditions as in the U.S.A.

LABORATORY EP TESTING MACHINES

In considering the possibility of using small laboratory EP testing machines for predicting the performance of oils in service, it is necessary to keep in mind the two quite distinct and often conflicting

requirements, namely high-speed and low-speed high-torque, already discussed.

For the high-speed conditions, where failure resulted from scoring or scuffing, it seemed reasonable to suppose that machines which gave pure sliding, *e.g.* the four-ball, Almen, and Timken machines,[11] need not be ruled out of consideration, whereas such machines were unlikely to be of use for evaluating low-speed high-torque performance. In any event it seemed that at least two distinct tests should be employed, one to correlate with high-speed conditions and the other with low-speed high-torque conditions, it being unreasonable to expect, as Blok has inferred,[3] one machine to give the answer to both problems.

Dealing first with the low-speed high-torque problem, suggestions have been made for using the SAE machine,[11] suitably modified, to predict the performance of oils in the L-20 test. Eastman and co-workers,[12] by reducing the main shaft speed, altering the rubbing ratio, and modifying the machine so that hot oil could be continuously circulated, obtained a fair degree of correlation based on the weight losses of the test cups and visual examination of their surfaces. McKee and co-workers,[13] using a similarly modified SAE machine and measuring rate of wear and changes in surface roughness of the test cups, were able to demonstrate marked differences in the behaviour of FS-VVL-761 and MIL-L-2105 type oils, while Manteuffel and Stucker,[14] using a modification of the Eastman procedure, have done some work on phosphate-coated test cups.

Turning now to the consideration of high-speed high-load conditions of operation, the SAE machine, running at 1000 rev/min or at 750 rev/min with a 14·6 : 1 rubbing ratio, is still used by some motor manufacturers for evaluating hypoid gear oils. It suffers, however, from the disadvantage of poor reproducibility, failure loads being affected greatly by minor differences in the surface finish of the rings. The difficulty in obtaining supplies of test cups of consistent quality militates against the successful use of this machine, but fortunately, in the modified test procedure designed to simulate low-speed high-torque conditions, these differences appear to be less critical. The four-ball machine, on the other hand, is one which gives a fair degree of reproducibility and on which a number of different criteria can be determined. Of these, Hughes [15] considers the mean Hertz load and flash temperature parameter [16] to be the best for predicting the performance of hypoid gear oils. One disadvantage of the conventional laboratory EP test procedures is that in all cases where the loading is increased this is done gradually, whereas in the L-42 axle test and in practice in the field the load may be applied suddenly. Some form of laboratory shock test therefore appeared to be desirable.

Towle [2] has quoted results obtained using the Almen, Falex, Timken, SAE, and four-ball machines on various types of hypoid gear oil and concluded that these machines are " unlikely to correlate with service experience " and that " different machines rate the oils in quite different orders." A careful analysis of Tables VII and IX of this paper, however, seemed to indicate that whilst the Falex and Timken machines obviously failed to correlate with performance under high-speed conditions, this was not true of the four-ball machine, on which nine oils having M.H.L. of about 70 or above all gave passes or borderline passes in the L-19 test, whilst two oils with substantially lower M.H.L. failed this test. This point was made by Withers in the discussion on Towle's paper. The Almen machine, using the normal test procedure, was obviously not sufficiently discriminating, whereas there was not sufficient evidence on the SAE machine one way or the other. None of the machines correlated with the L-20 high-torque test, but this was not surprising, since all the machines were operated at high speeds.

In view of the existing situation, it was decided to investigate further the possibility of using the four-ball machine to predict high-speed performance and a modified SAE machine test to predict low-speed high-torque performance. It was decided to supplement these tests with a novel shock loading test using the Almen machine, since this machine was the most easily adapted for the purpose. Details of the test procedures employed are given in the next section.

TEST PROCEDURES

1. The four-ball machine was used under normal conditions as described by West,[11] using a test period of one-minute duration, these tests being supplemented, in some instances, by determinations of mean Hertz load by the standard procedure.[17] Following the one-minute runs, the wear–load curves were plotted on log–log paper, the incipient seizure load, weld point, and mean wear scar diameters at certain fixed loads being read off from the curve and recorded.

2. The SAE machine was modified in a manner similar to that described by McKee and co-workers.[13] This involved removing the gears and replacing them with gears having 52 and 49 teeth respectively so as to give a 3·4 : 1 gear ratio or a 2·4 : 1 ratio of rubbing to rolling at the contacting surfaces and providing the machine with an oil circulating system. This consisted of a cylindrical metal oil reservoir capable of being heated externally by means of an electric heating tape and fitted with a cooling coil (water), a motor-driven pump, and a $\frac{1}{4}$-inch copper pipe leading to the top of the upper test cup, which was covered by a special splash guard. The oil box of the machine was fitted with two $\frac{3}{8}$-inch overflow pipes leading into a $\frac{3}{4}$-inch drain pipe through which the oil flowed back

into the reservoir, the overflow pipes being sited so that the lower test cup was partially immersed. Between the oil reservoir and the pump a magnetic filter was fitted to remove wear debris. Prior to this being fitted, trouble was experienced due to metallic particles circulating in the oil and invalidating the test results. In the earlier work the oil pipe leading from the pump was wound with electric heating tape and the temperature of the oil in the oil box measured by means of a thermocouple attached to a pyrometer, the oil temperature being maintained approximately constant by manual adjustment of a " Simmerstat " controller in series with the heating tape on the inlet pipe. It was found that the temperature could be controlled reasonably well and that there was often no need to heat the oil reservoir once the oil temperature had been raised initially to the required value. In later work the heating tape on the oil pipe was removed and replaced by two 250-watt infra-red lamps directed on to the oil box. This enabled still better temperature control to be achieved. As these tests resulted after a time in severe wear of the bearings of the machine, these were replaced by bronze bearings.

The differences in test conditions between the Eastman [12] (Monsanto) method, the McKee [13] method, and the authors' (Hayes) method are summarized in Table III.

It should be borne in mind that whereas the Monsanto and McKee test procedures were designed to correlate with the L-20 test, the Hayes method was designed primarily with the L-37 test in view. The oil temperature was accordingly fixed at 275° F, the same as in the L-37 test, and the load at 250 lb, which was the highest load at which the authors were able to work without running into trouble due to slipping of the test cups on their tapered spindles. McKee and co-workers tested five different MIL-L-2105 oils at four different loads and found that whilst all five oils behaved satisfactorily at 135 lb, two of them resulted in high wear of the test cups at 225 lb, while at 180 lb one of these oils was beginning to produce a higher than normal wear rate, an effect enhanced when the oil temperature was raised from 225° to 250° F. It seemed therefore that 180 lb was somewhere about the critical load for correlation with the L-20 test and that 250 lb would therefore be more than adequate for screening oils for the L-37 test, where the loading was approximately 1·3 times that of the L-20 test.

Some tests were also carried out at lower loads and temperatures, results in all cases being assessed on the basis of weight losses of the test cups, visual assessment of their surface condition along the lines described by Eastman,[12] and a very approximate estimate of surface roughness using a surface roughness gauge.

3. The shock-load test on the Almen machine was performed by loading the machine up to 4000 p.s.i. in the normal manner as described by West.[11] The pan and weights were then lifted manually a distance of 4 inches and suddenly released, three successive " bumps " being performed at 5-second intervals, at each load. This procedure was then repeated at successive load increments of 1000 p.s.i. until seizure took place. Tests were carried out in duplicate or triplicate, and agreement was fairly good in general, although occasional freak results were obtained. It was found necessary to allow the machine to cool down between tests.

TABLE III

Modified SAE Machine Test Procedures

	Monsanto Method	McKee Method	Hayes Method
Main shaft speed, rev/min	264	500	500
Rubbing ratio	3·4 : 1	3·4 : 1	3·4 : 1
Break-in run:			
Duration, minutes	30	None	30
Load, lb	50	—	50
Test run:			
Duration, hours	15	25	12
Load, lb	110	90, 135, 180, and 225	250 (generally)
Oil temperature, ° F	200–250 (cycling)	225 and 250	275 (generally)
Quantity of oil used	Lower test cup half immersed; oil topped up as necessary	¼ gallon, circulated at about 500 g/minute	As McKee method

SUMMARY OF OILS TESTED

Allusion has already been made to a series of reference oils used in a co-operative research programme in the U.S.A. during the development of the L-42 high-speed axle test. These were SAE 90 oils containing differing amounts of the same additive and rated 0–90 to 15–90 according to the additive dosage present, 0–90 being the base oil without additive. Samples of the two oils 0–90 and 15–90 were obtained, and oils of intermediate composition were prepared by blending these in the appropriate proportions. In the CRC report,[7] the two oils are designated RGO-100-57 and RGO-115-57 respectively, and it was concluded

that an oil of 10–90 level was required to pass the L-42 test, an oil of 8–90 level failing to prevent scoring in this test. The MIL-L-2105 performance level (L-19 test) lay between 5–90 and 6–90, while 15–90 was capable of passing the most severe scoring tests in existence.

A number of other oils were tested, all falling within the SAE 90 viscosity classification, details of these oils being summarized in Table IV. Alongside a general description of the nature of the additives present in these oils is a statement of the approximate percentages of chlorine, sulphur, and phosphorus introduced into the oils by the additives used, including both EP additives and anti-oxidants.

TABLE IV

Details of SAE 90 Hypoid Gear Oils

Oil	Additives present	Percentage of active elements present in the oil		
		Cl	S	P
A	Approved MIL-L-2105 additive in recommended amount	2·0	0·42	0·03
B	„ MIL-L-002105A „ „ „	1·4	1·3	0·40
C	Different approved MIL-L-002105A additive in recommended amount	1·6	1·5	0·29
D	FS-VVL-761 type additive as used for factory fills	4·0	0·28	Nil
E	Experimental additive containing chlorinated aliphatic hydrocarbon, sulphur compound, and a phosphosulphurized wool grease derivative	2·1	0·44	0·05
F	Experimental additive mixture comprising a chlorinated aliphatic hydrocarbon and a sulphur compound with an active phosphorus compound and corrosion and oxidation inhibitors	1·6	0·80	0·28
G	As in Oil F without active phosphorus compound	1·6	0·80	0·04
H	„ „ F „ sulphur compound	1·6	0·08	0·28
I	„ „ F „ chlorine compound	Nil	0·80	0·28
J	„ „ F with the sulphur compound replaced by a sulphur-and-chlorine containing compound + a synergistic additive affecting shock-loading properties	1·9	0·81	0·30
K	As in Oil F with the chlorinated aliphatic hydrocarbon replaced by a chlorinated aromatic hydrocarbon	2·6	0·86	0·32
L	Of same general type as Oil F but containing a different chlorine compound and a sulphur-and-chlorine containing compound with an active phosphorus compound and corrosion and oxidation inhibitors	1·9	0·74	0·40
M	As in Oil F, but containing different chlorine, sulphur, and phosphorus compounds	1·8	0·80	0·38
N	Chlorinated aliphatic hydrocarbon only	2·1	Nil	Nil
O	As in Oil N + sperm oil	2·1	Nil	Nil
P	„ „ N + sulphurized sperm oil	2·1	0·70	Nil
Q	„ „ N + phosphosulphurized sperm oil	2·1	0·50	0·05
R	„ „ P + organic phosphite ester	2·1	0·70	0·04
S	„ „ F, but active phosphorus compound substituted by tricresyl phosphate	1·6	0·80	0·25

HIGH-SPEED TEST PROCEDURES (FOUR-BALL MACHINE)

The results obtained, using the four-ball machine, on the series of reference oils described above are summarized in Table V, together with results on certain other oils of known performance.

The wear–load curves for the one-minute runs on the four-ball machine are plotted on Fig 1 (tests 1–5) and Fig 2 (tests 6–10)

From a study of Fig 1 in conjunction with Table V, it was apparent that neither incipient seizure loads, weld loads, nor wear scar diameters at the selected loads sufficiently differentiated between the reference oils 5–90 to 15–90. The reason for this was apparent from Fig 1. The oils containing the higher proportions of additives gave wear/load curves having more than one break, and incipient seizure took place at much the same point with oils 8–90, 10–90, and 15–90. Above 240 kg there was little difference in the behaviour of the four additive-containing reference oils, differences in weld loads probably being due to minor differences in the balls used for the tests. Since reference oil 15–90 passed all known axle tests, including the most severe shock tests, it may be that on the four-ball machine we need not concern ourselves with loads exceeding about 240 kg.

The main distinction between the four reference oils clearly lay in the load at which a sudden major increase in wear scar diameter took place and in the wear increment at this point. Some indications of these criteria were given by the "1-mm load," *i.e.* the load at which the scar diameter reached 1 mm, and by the maximum wear/load increase over the whole curve. The latter was expressed in mm/kg and was obtained by taking the scar diameter increase over a 20-kg range enclosing the steepest part of the curve.

The mean Hertz load integrates all the factors in-

TABLE V

Four-Ball Machine Tests

Test No.	Oil	Standard one-minute test			Mean wear scar dia at			Mean Hertz load test	
		Incipient seizure load, kg	Approx 2½-second seizure delay load, kg	Weld point, kg	100 kg	200 kg	300 kg	M.H.L.	Flash temperature parameter, kg
1	0–90	55/60	55/60	160	2·7	—	—	22·2	123
2	5–90	105/110	140/145	400	0·41	1·70	2·2	65·9	280
3	8–90	125/130	135/140	490	0·40	1·55	2·0	80·8	305
4	10–90	120/130	170/175	450	0·40	1·70	2·1	77·2	420
5	15–90	120/130	190/200	450	0·40	0·89	1·9	99·2	370
6	Oil A	145/150	130/140	400	0·40	1·50	2·3	78·5	341
7	Oil B	105/110	180	470	0·38	1·31	1·8	91·5	378
8	Oil C	105/110	170/180	380	0·44	1·25	1·6	95·9	340
9	Oil D	100/110	170/180	440	0·45	0·90	1·4	93·5	448
10	Oil F	115/125	120/130	440	0·44	1·40	1·9	90·6	385

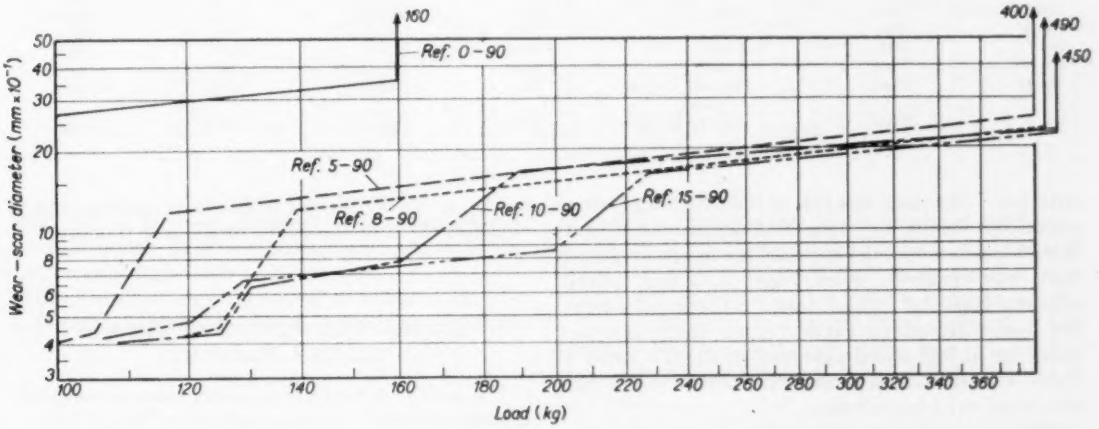

FIG 1

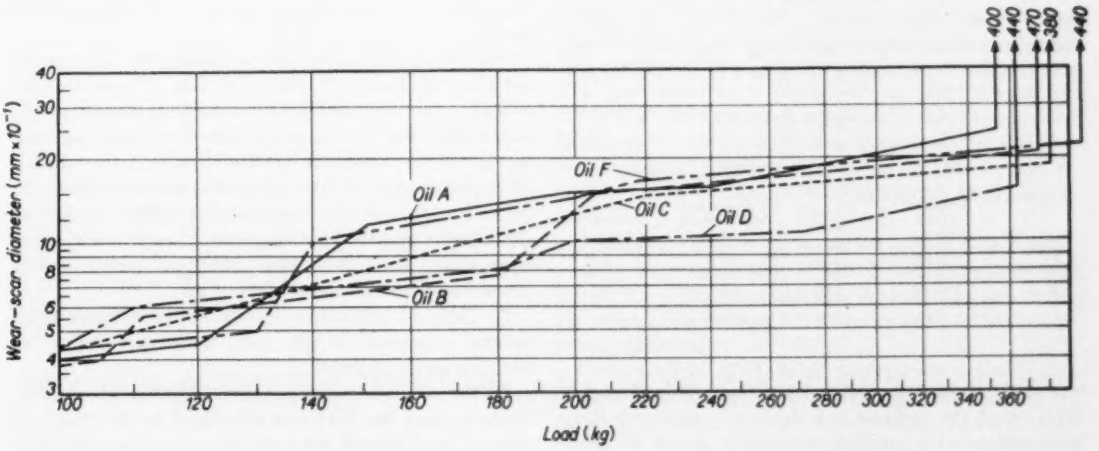

FIG 2

volved, including incipient seizure load and weld load. The M.H.L. of the reference oils thus followed the expected trend but did not distinguish between the oils so effectively as the " 1-mm load " and rated 8–90 and 10–90 equal within the limits of the repeatability of the test, as quoted by Hughes.[15] With oils A, B, C, D, and F, all containing different additives, the M.H.L. did not appear to be a very reliable criterion. The same was true of the flash temperature parameter, whilst the 2½-second seizure-delay load, though much more relevant than the incipient seizure load, was evidently, from Table V, a less reliable criterion than the " 1-mm load." These conclusions are demonstrated in Table VI, in which the performance in high-speed axle tests of the oils listed in Table V is quoted, together with the more relevant data from the four-ball tests.

It would be unwise to make too definite predictions based on the limited amount of evidence so far obtained, but it would appear that oils having a " 1-mm load " of 160 kg or above and a maximum wear/load increase of not more than about 0·03 mm/kg should stand a good chance of passing the L-42 test.

It would clearly be desirable to supplement this work by testing oils of known L-42 performance containing as many different additives as possible, and to establish the reproducibility of the test procedure.

TABLE VI

Lubricant	Performance in axle tests		Four-ball test data			Max wear/ load increase, mm/kg
	L-19	L-42	M.H.L.	2½-second seizure delay, kg	" 1-mm load," kg	
Ref. oil 0–90	Fail	Fail	22·2	55/60	57	0·105
Ref. oil 5–90	Borderline fail	Fail	65·9	140/145	110	0·042
Ref. oil 8–90	Pass	Borderline fail	80·8	135/140	135	0·037
Ref. oil 10–90	Pass	Pass	77·2	170/175	170	0·030
Ref. oil 15–90	Pass	Pass	99·2	190/200	205	0·027
Oil A	Pass	Fail	78·5	130/140	145	0·015
Oil B	Pass	Pass	91·5	180	190	0·022
Oil C	Pass	Pass	95·9	170/180	170	0·010
Oil D	Pass	Almost certain pass	93·5	170/180	205	0·020
Oil F	Pass	Fail (near miss)	90·6	120/130	145	0·030

It is necessary to consider the maximum wear/load increase as well as the " 1-mm load," as otherwise it would be possible to be seriously misled, since some oils survive quite high loads without any seizure taking place, after which a small load increment produces sudden seizure with large wear scars. This phenomenon is illustrated in Table VII, in which Oil F is compared with similar compositions (Oils H and I) from which the sulphur and chlorine compounds have been respectively omitted and which would be quite unsuitable as hypoid gear lubricants.

TABLE VII

Lubricant	Four-ball test			
	Incipient seizure load, kg	" 1-mm load "	Max wear/ load increase, mm/kg	Wear scar dia at 160 kg
Oil F . .	115/125	145	0·030	1·20
Oil G . .	<120	167	0·015	0·85
Oil H . .	150/160	155	0·065	1·75
Oil I . .	150/160	157	0·050	1·50
Oil J . .	<120	156	0·033	1·30

HIGH-SPEED TEST PROCEDURES (ALMEN MACHINE)

The results of Almen tests on the same series of oils quoted in Table V are summarized in Table VIII.

It is evident from this table that even MIL-L-2105 oils withstood the full load under the standard test conditions, so that this test was valueless for distinguishing between hypoid gear oils of different EP levels.

The shock test appeared to distinguish adequately between MIL-L-2105 oils and oils of greater EP activity, but the repeatability of the tests as applied to the reference oils was poor, which was disappointing in view of the consistent results obtained on a number of experimental oil blends, a selection of which are quoted in Table IX. The fact that reference oil 8–90 sustained a greater load than oils B and C containing approved MIL-L-002105A additives cast serious doubts on the usefulness of this test.

In Table IX are quoted Almen shock test results on several experimental oils with comparative data on the four-ball machine.

Of the oils listed in this table, only Oil L would be likely to pass the L-42 test as judged by the four-ball criteria, and this oil did not sustain as high a load on the Almen machine as Oils J and M.

One point worthy of comment was the effect of quite small amounts of a synergistic additive on the Almen shock test breakdown load. The addition of as little as 0·1 per cent of this additive to Oil F raised this load to over 15,000 p.s.i., whilst its omission from a blend similar to Oil J resulted in a drop in breakdown load from over 15,000 to 11,000 p.s.i. No comparable effect has so far been observed on the four-ball machine, although there is a tendency for the wear scar diameters at high loads to be reduced.

The Almen machine appeared to be more sensitive to the omission of the chlorine compound, whilst the four-ball machine reacted more adversely to the omission of the sulphur compound (compare Oils F, H, and I). The influence of the chlorine compound was evident also when comparing the Almen test results on Oils F, K, L, and M, all of which contained different chlorine compounds.

TABLE VIII
Almen Machine Tests

Test No.	Oil	Standard breakdown test. Failure load, p.s.i.	Shock test. Failure load, p.s.i.				
			Run 1	Run 2	Run 3	Run 4	Run 5
1	0–90	4,000	—	—	—	—	—
2	5–90	>15,000	4,000	13,000	4,000	>15,000 (heavy wear)	>15,000
3	8–90	>15,000	>15,000	>15,000	>15,000	—	—
4	10–90	>15,000	10,000	>15,000	>15,000	>15,000	—
5	15–90	>15,000	>15,000	14,000	>15,000	—	—
6	Oil A	>15,000 (with heavy wear)	Variable results between 4,000 and 6,000				
7	Oil B	>15,000	15,000	15,000	—	—	—
8	Oil C	>15,000	9,000	10,000	9,000	—	—
9	Oil D	>15,000	15,000	>15,000	—	—	—
10	Oil F	>15,000	9,000	10,000	11,000	—	—

TABLE IX

Test No.	Oil	Almen shock test		Four-ball machine test	
		Failure load p.s.i.		"1-mm load," kg	Max. wear/load increase, mm/kg
		Run 1	Run 2		
1	Oil F	9,000	10,000	145	0·030
2	Oil G	10,000	10,000	167	0·015
3	Oil H	8,000	9,000	155	0·065
4	Oil I	7,000	7,000	157	0·050
5	Oil J	>15,000	>15,000	156	0·033
6	Oil K	8,000	7,000	158	0·044
7	Oil L	13,000	14,000	184	0·012
8	Oil M	>15,000	>15,000	165	0·045

LOW-SPEED HIGH-TORQUE PROCEDURE (SAE MACHINE)

A first series of tests were carried out under the conditions described with a load of 200 lb (scale reading) and an oil temperature of 225° ± 5° F, designed to correlate with the L-20 test. The results are summarized in Table X.

These tests were encouraging inasmuch as the type of failure experienced resembled that obtained in low-speed high-torque axle tests. Furthermore, Oil A, which passed the L-20 test, gave low wear and no more than light rippling in the modified SAE test, whilst Oil D, which was of the FS-VVL-761 type and failed the L-20 test, gave high wear coupled with ridging and pitting. Unfortunately, however, Oil E, which performed well in the SAE test, failed the L-20 test by a considerable margin due to heavy rippling of the pinion gear and heavy ridging of both pinion and ring gears.

One striking fact which emerged from the tests in Table X was the profound difference in behaviour between oils which contained phosphorus and those which did not. This pointed to the fact that the formation of a chemical EP film on the metal surface was needed to produce adequate resistance to surface deformation under low-speed high-torque conditions. This was possibly a phosphide or phosphide–metal eutectic of the type postulated by Beeck, Givens, and Williams.[18] No benefit was conferred by the use of long-chain polar additives, as in Oils O and P, which would merely provide adsorbed films on the surface.

A further series of tests carried out at 250 lb load, with an oil temperature of 275° F, are summarized in Table XI. The compositions included in this table are a selection of many that have been tested under these conditions.

With an SAE 90 base oil blend, failure took place even at 100 lb load, due to scuffing, accompanied by rippling, a weight loss of 708 mg being obtained after 5 hours. Failure occurred after 1 hour at 120 lb load and instantly at 180 lb.

With a large number of oils tested it was found that the bulk of the wear took place in the first 5 hours.

It was clear from Table XI that by increasing the severity of the test it was possible to distinguish between Oils A and E, which had behaved similarly before. This was in line with the experience of McKee and co-workers, already referred to. On the other hand, Oils B and C, containing additives used in the proportions recommended by the manufacturers to pass the L-37 test, exhibited a very poor performance in this test, which suggested that the test conditions chosen were rather too severe.

On the other hand, several oils containing active phosphorus compounds performed very satisfactorily even under these strenuous conditions, and one of these, Oil F, successfully passed the L-37 test. This suggested that these oils held a good deal in reserve with respect to low-speed high-torque performance.

The effect of replacing the active phosphorus compound in Oil F by tricresyl phosphate, a relatively inactive material, is demonstrated in Test No. 13, high wear and heavy ridging being obtained. The significance of this will be discussed in the final section of the paper.

It should be pointed out here that although Oil A apparently gave a very satisfactory result in this test

TABLE X

Modified SAE Machine Tests

Load, 200 lb
Oil temp, 225° F

Test No.	Lubricant	Test duration, hours	Test cup wt loss, mg			Change in surface roughness	Condition of test cup surfaces
			Top	Bottom	Total		
1	Oil A	12	15·5	14·8	30·3	Decreased	Burnishing or slight rippling
2	Oil D	12	180	409	589	Increased	Ridging and rippling; one ring pitted
3	Oil E	12	16·0	23·6	39·6	Little change	Almost as new
4	Oil N	6	—	189	—	Much increased	Severe ridging; one ring pitted
5	Oil O	5	390	147	537	,, ,,	,, ,, ,,
6	Oil P	7	1100	279	1379	,, ,,	,, ,, ,,
7	Oil Q	12	13·2	8·8	22	Decreased	Smoothing; one ring pitted
8	Oil R	12	7·8	16·1	23·9	Little change	Light/moderate ridging and rippling
9	Base oil (SAE 90)		Scuffed at 190 lb while load was being applied				

TABLE XI

Modified SAE Machine Tests

Load, 250 lb
Oil temp, 275° F

Test No.	Lubricant	Test duration, hours	Test cup wt. loss, mg			Change in surface roughness	Condition of test cup surfaces
			Top	Bottom	Total		
1	Oil A	12	9·4	11·8	21·2	Decreased	Slight burnishing
2	Oil B	9	1625	364	1989	—	Heavy wear and ridging
3	Oil C	2·5	1263	226	1489	—	Heavy wear, ridging, and scoring
4	Oil E	12	63	396	456	—	Moderate ridging (top). Smoothing and light rippling (bottom)
5	Oil F	12	20·6	16·4	37	Top decreased. Bottom increased	Burnishing (top). Light ridging (bottom)
6	Oil G	4	2811	347	3158	—	Heavy ridging and rippling. Metal removal at edges
7	Oil J	5	21·8	16·3	38·1	Decreased	Slight burnishing
8	Oil K	5	30	27	57	,,	Moderate burnishing
9	Oil L	5	31	20	51	,,	,, ,,
10	Oil M	5	21·5	20·5	42	,,	Light ridging (both)
11	Ref. oil 5–90	0·5	159	46	205	—	Ridging and metal pick-up
12	Ref. oil 10–90	2·5	320	203	523	—	Deep ridging and metal removal from lower ring
13	Oil S	5	285	477	732	—	Heavy ridging and top ring badly pitted

as far as the condition of the test cups were concerned, very heavy sludging of the oil was experienced and black deposits were formed in the oil box. Evidently the additive in this oil was thermally unstable at 275° F, and this, it was understood, was the reason for its failure in the L-37 test. Sludge was not entirely absent from any of the oils tested, but nothing comparable to Oil A was experienced.

FILM FORMATION STUDIES USING RADIOACTIVE TRACER TECHNIQUES

In some early work Clark *et al.*[19] investigated the extent of sulphide film formation on various metal alloys using an S^{35} sulphurized olefinic hydrocarbon. Their work showed that adherent sulphur-bearing films were laid down even at low temperatures (88° C). Work has been done by Borsoff [20] on a " four square " gear rig using an irradiated gear mating with an inert gear. Measurements were taken of the radiation appearing on the inert gear and also in the lubricant (due to wear debris). Mineral oils, certain synthetic oils, and EP mineral oils were tested. It was noted that gear wear was almost entirely due to scoring when undoped oils were used. When chlorinated wax was used in mineral oils, wear was by chemical corrosion, whereas with dibenzyl disulphide wear was by scoring. Similarly, tricresyl phosphate gave gradually increasing wear, said to be due to abrasion. Interesting work has since been done by Borsoff and co-workers [21] on the same rig using S^{35} labelled dibenzyl disulphide in an SAE 30 mineral oil. Measurement was made of the radioactivity appearing on the gear teeth surfaces. From these measurements it was noted that the chemical film thickness increased with increase in load, but was virtually independent of time. A steady state thickness was established for each operating condition. Experiments were also conducted by immersing preheated steel strips in the radioactive oil, measuring the thickness of the film deposited, and plotting this against time. The reaction was thought to be autocatalytic and was time-dependent under the conditions studied.

Further work using labelled compounds has now been done with a view to advancing our understanding of the mechanism by which EP additives act. In the present series of experiments additives were dissolved in mineral oil (brightstock of viscosity about 35 cS at 210° F) singly or in combination. In each case a small mild steel disk was totally immersed in the oil, contained in a test tube, and the assembly held at one of three temperatures (100° C, 150° C, or 200° C) in an oven, radioactivity on the surface of the disk being measured from time to time. The disks were thoroughly rinsed in benzene prior to each measurement to remove oil and any loose deposit.

The following compounds were prepared or obtained:

Reference letter	Compound (or element)	Labelled
S_1	Sulphur	S^{35}
S_2	Dibenzyl disulphide	S^{35}
P_1	Tricresyl phosphate	P^{32}
P_2	Active phosphorus compound	P^{32}
Cl_1	Chlorinated paraffin wax	Inert

S_1, P_1, and P_2 were prepared by the Radiochemical Centre, Amersham, while S_2 was synthesized in the laboratory at Hayes from benzyl chloride, inactive sodium sulphide, and radioactive sulphur. Only half the sulphur present in this compound was therefore labelled. This was allowed for in calculating the sulphur-bearing film thickness in the ensuing tables, the observed figure being doubled in this case.

Mineral oil blends were prepared as shown in Table XII.

TABLE XII

Blend No.	% Additive present					% E.P. element		
	S_1	S_2	P_1	P_2	Cl_1	S	P	Cl
1	0·78	—	—	—	—	0·78	—	—
2	—	3·0	—	—	—	0·78	—	—
3	0·78	—	—	—	4·0	0·78	—	1·6
4	—	3·0	—	—	4·0	0·78	—	1·6
5	—	—	3·0	—	—	—	0·25	—
6	—	—	—	1·5	—	—	0·28	—
7	—	—	3·0	—	4·0	—	0·25	1·6
8	—	—	—	1·5	4·0	—	0·28	1·6
9	0·78	—	3·0	—	—	0·78	0·25	—
10	0·78	—	—	1·5	—	0·78	0·28	—
11	—	3·0	3·0	—	—	0·78	0·25	—
12	—	3·0	—	1·5	—	0·78	0·28	—
13	0·78	—	3·0	—	4·0	0·78	0·25	1·6
14	0·78	—	—	1·5	4·0	0·78	0·28	1·6
15	—	3·0	3·0	—	4·0	0·78	0·25	1·6
16	—	3·0	—	1·5	4·0	0·78	0·28	1·6

TABLE XIII

Blend	Temperature, °C	Hours	Mg S^{*35}/sq cm	Mg P^{32}/sq cm
2	200	3	Nil	—
		27	0·03	—
		106	0·59	—
		133	>0·9	—
		199	>0·9	—
		230	>0·9	—
10	200	3	—	0·023
		27	—	0·043
		106	—	0·013
		133	—	0·021
		199	—	0·049
		230	—	0·038

From the results obtained it became evident that certain films built up steadily with time, reaching an approximately constant thickness. Others first built up and then were partially removed, only to build up again, thus undergoing a cycle of changes. In this case, however, it was noticed that a certain minimum adherent film thickness always remained. Examples of the two types of results are given in Table XIII.

In Table XIV there is given the approximate thickness of each adherent film as mg radioactive element per square centimetre from the measurement of activity at the surface of each steel disk. This figure was necessarily somewhat difficult to estimate with the type of film build-up sometimes experienced (which is discussed above), although the results obtained were accurate and reliable. Table XIV is probably an oversimplification, but it does serve to illustrate the points under discussion in the paper.

With oils containing either sulphur or phosphorus with or without chlorine the disks were counted with an end window Geiger–Müller tube. Where sulphur and phosphorus occurred together the disk was counted as before, but with and without an absorber of 10 thou of aluminium. It can be shown that this absorber will absorb all radiation due to S^{35} but only attenuate the radiation due to P^{32} by a small factor (about $\frac{1}{3}$). This enabled estimation of both films in the presence of each other.

Table XIV is divided into four in order that individual films and the effect of other additives upon them may be studied. Sections 1 and 2 give results for the additives taken either singly or in pairs. Sections 3 and 4 relate to the additives taken three at a time. Figures in brackets in the table are somewhat in doubt, as the tests concerned were interrupted. Those results marked with an asterisk were characterized by a fluctuating film thickness of the type above described.

TABLE XIV

Section 1—Phosphorus-Bearing Film

Blend No.	Additive(s)	Film thickness (mg P^{32}/sq cm)		
		At 100° C	At 150° C	At 200° C
5	P_1	Nil	Nil	<0·006
6	P_2	0·04 *	0·06	0·06
7	$P_1 + Cl_1$	Nil	Almost nil	Almost nil
8	$P_2 + Cl_1$	0·075	0·06	0·11
9	$P_1 + S_1$	Nil	Nil	0·008
10	$P_2 + S_1$	0·075 *	0·056	0·057 *
11	$P_1 + S_2$	<0·005	Nil	Almost nil
12	$P_2 + S_2$	0·056	(0·084)	0·112

Section 2—Sulphur-Bearing Films

Blend No.	Additive(s)	Film thickness (mg S^{35}/sq cm)		
		At 100° C	At 150° C	At 200° C
1	S_1	Nil	0·4	0·75
2	S_2	Nil	0·03	>3·6
3	$S_1 + Cl_1$	Nil	Nil	Nil
4	$S_2 + Cl_1$	Nil	Nil	<0·14
9	$S_1 + P_1$	Nil	0·26	0·1
10	$S_1 + P_2$	Nil	Nil	<0·05
11	$S_2 + P_1$	Nil	0·2	Almost nil
12	$S_2 + P_2$	Nil	(Nil)	Nil

Section 3—Phosphorus-Bearing Films

Blend No.	Additive(s)	Film thickness (mg I^{32}/sq cm)		
		At 100° C	At 150° C	At 200° C
5	P_1	Nil	Nil	<0·006
6	P_2	0·04 *	0·06	0·06
13	$S_1 + P_1 + Cl_1$	Nil	0·01	<0·01
14	$S_1 + P_2 + Cl_1$	0·4 *	(0·3) *	1·0 *
15	$S_2 + P_1 + Cl_1$	Nil	Nil	0·18
16	$S_2 + P_2 + Cl_1$	0·2 *	0·2 *	0·4 *

Section 4—Sulphur-Bearing Films

Blend No.	Additive(s)	Film thickness (mg S^{35}/sq cm)		
		At 100° C	At 150° C	At 200° C
1	S_1	Nil	0·4	0·75
2	S_2	Nil	0·03	>3·6
13	$S_1 + P_1 + Cl_1$	Nil	<0·1	<0·1
15	$S_2 + P_1 + Cl_1$	Nil	Nil	0·21
14	$S_1 + P_2 + Cl_1$	Nil	Nil	<0·1
16	$S_2 + P_2 + Cl_1$	Nil	Nil	>3·6

From the above table certain facts were apparent. These may be stated as follows:

Section 1

1. The active phosphorus compound attacked the metal at all three temperatures, whilst the tricresyl phosphate had no action below 200° C. Even at this temperature the metal was attacked only to a small extent.

2. Attack by the tricresyl phosphate was not promoted by any of the chlorine or sulphur-bearing compounds studied.

3. Attack by the active phosphorus compound was not significantly decreased by the presence of the other compounds studied, but was materially increased at 200° C by both chlorine and sulphur compounds.

Section 2

1. Attack by sulphur increased markedly with temperature, and the same was true of dibenzyl disulphide.

2. The active phosphorus compound and the chlorinated compound reduced the attack due to combined and free sulphur very materially at the higher temperatures.

3. Tricresyl phosphate appeared to promote attack by dibenzyl disulphide at 150° C, but to inhibit it at 200° C.

Section 3

1. The action of tricresyl phosphate on steel was little affected by the presence of the other compounds except in the case of blend No. 15, where there was a surprising increase in activity at 200° C.

2. The presence of both sulphur and chlorine promoted attack at all temperatures by the active phosphorus compound.

Section 4

1. The formation of a sulphur-bearing film from sulphur was materially reduced in the presence of combined phosphorus and chlorine compounds.

2. Attack by dibenzyl disulphide was also materially reduced in every case except with blend No. 16 at 200° C.

In view of the importance of the above conclusions some further work was done to determine:

(*a*) if a sulphur-bearing film could be replaced by chlorine from an oil solution of the chlorinated compound;

(*b*) if a chlorine-bearing film could be replaced by a phosphorus-bearing film in the same way.

Using disks pre-coated with either a sulphur or chlorine-bearing film, the level of radioactivity at the surface of the disks was measured from time to time with the following results:

(*a*) At all three temperatures studied (100° C, 150° C, and 200° C) there was continuous removal of sulphur-bearing film, reaching a steady state at about 30 per cent removal.

(*b*) Phosphorus in the active phosphorus compound vigorously displaced the chlorine-bearing film. Phosphorus in tricresyl phosphate failed to displace the chlorine-bearing film at 100° C and 150° C, and only succeeded to a very limited extent at 200° C.

Actually, it proved quite easy to determine visually the nature of the film on the surface. The sulphur-bearing film, probably iron sulphide, was blackish in appearance; the phosphorus-bearing film, probably a phosphide, was dark grey; and the chlorine-bearing film was a light reddish brown.

DISCUSSION

Bowden and Tabor [22] have suggested that the so-called " extreme pressure " lubricants might be more appropriately named " extreme temperature " lubricants, because it is the very high temperatures which are developed locally which render necessary the use of chemically-active additives. At these high local temperatures, oil films and films of polar additives, such as fatty acids or metal soaps, would be thermally degraded.

Davey,[23,24] using the four-ball machine, has produced evidence showing that iron chloride is formed when chlorine-bearing additives are used as EP additives, iron sulphide being formed from sulphur compounds. Prutton, Turnbull, and Dlouhy [25] have made a very comprehensive investigation of the mechanism of action of combinations of sulphur and chlorine compounds. They showed that ferrous chloride was the predominating film formed in such circumstances, but that this film was formed much more rapidly when active sulphur compounds were present, than when only chlorine compounds were present. They postulated that iron sulphide was first formed by interaction of the metal with the sulphur compound, after which the chlorine compound reacted with the iron sulphide, yielding ferrous chloride and sulphur, this theory being supported by considerable experimental evidence. They concluded that a film of ferrous chloride was formed at the contact points of the gear teeth and that as temperatures became higher the resistance of the chloride films to shear became small, possibly due to fusion (melting point of $FeCl_2$ = 690° C) or to the low shear strength of the solid film at high temperatures.

The fact that mixtures of chlorine and sulphur-bearing additives yield primarily chloride films and not sulphide films has been amply confirmed by our own experiments using radioactive tracers.

An interesting point that emerged from the radioactive tracer experiments was that a much greater sulphide film thickness was produced at 200° C on the steel by dibenzyl disulphide than by elementary sulphur, whereas at 150° C the converse was true. It would appear that this must be due to the decomposition of the dibenzyl disulphide at the metal surface at 200° C, yielding chemically-active sulphur. The decomposition of this compound on ferrous surfaces has been discussed by Davey and Edwards.[26] In the presence of a compound such as a chlorinated paraffin wax this would result in the rapid formation of a ferrous chloride film at temperatures of this order, which may account for the success of this type of lubricant under high-speed conditions.

Prutton, Turnbull, and Dlouhy [25] have shown that iron sulphide films from active sulphur additives form much more rapidly than ferrous chloride films from active chlorine additives, when these additives are used singly. It may therefore be assumed that no appreciable ferrous chloride film will be formed from oils containing mixtures of active sulphur and chlorine compounds at temperatures below that at which the sulphur compound attacks the metal. Thus, ferrous chloride film formation from dibenzyl disulphide/chlorinated wax combinations should be rapid at 200° C but negligible at 150° C, whilst with sulphur/chlorinated wax combinations it should be appreciable at both temperatures. In neither case would any ferrous chloride be formed at 100° C.

It was very significant that oils containing the active phosphorus compound P_2 all produced an appreciable amount of phosphorus-bearing film even at 100° C, *i.e.* at a temperature well below that at which ferrous chloride would be formed. It was equally significant that all oils containing this additive gave good results in the modified SAE machine test (Oils F, J, K, L, M).

Finch and Spurr [27] have pointed out that although the total heat energy developed between sliding surfaces is proportional to the product of load and sliding speed, the temperature rise at the areas of contact is primarily determined by the velocity. Local temperatures are therefore likely to be considerably higher

In Table XIV there is given the approximate thickness of each adherent film as mg radioactive element per square centimetre from the measurement of activity at the surface of each steel disk. This figure was necessarily somewhat difficult to estimate with the type of film build-up sometimes experienced (which is discussed above), although the results obtained were accurate and reliable. Table XIV is probably an oversimplification, but it does serve to illustrate the points under discussion in the paper.

With oils containing either sulphur or phosphorus with or without chlorine the disks were counted with an end window Geiger–Müller tube. Where sulphur and phosphorus occurred together the disk was counted as before, but with and without an absorber of 10 thou of aluminium. It can be shown that this absorber will absorb all radiation due to S^{35} but only attenuate the radiation due to P^{32} by a small factor (about $\frac{1}{3}$). This enabled estimation of both films in the presence of each other.

Table XIV is divided into four in order that individual films and the effect of other additives upon them may be studied. Sections 1 and 2 give results for the additives taken either singly or in pairs. Sections 3 and 4 relate to the additives taken three at a time. Figures in brackets in the table are somewhat in doubt, as the tests concerned were interrupted. Those results marked with an asterisk were characterized by a fluctuating film thickness of the type above described.

TABLE XIV

Section 1—Phosphorus-Bearing Film

Blend No.	Additive(s)	Film thickness (mg P^{32}/sq cm)		
		At 100° C	At 150° C	At 200° C
5	P_1	Nil	Nil	<0·006
6	P_2	0·04 *	0·06	0·06
7	$P_1 + Cl_1$	Nil	Almost nil	Almost nil
8	$P_2 + Cl_1$	0·075	0·06	0·11
9	$P_1 + S_1$	Nil	Nil	0·008
10	$P_2 + S_1$	0·075 *	0·056	0·037 *
11	$P_1 + S_2$	<0·005	Nil	Almost nil
12	$P_2 + S_2$	0·056	(0·084)	0·112

Section 2—Sulphur-Bearing Films

Blend No.	Additive(s)	Film thickness (mg S^{35}/sq cm)		
		At 100° C	At 150° C	At 200° C
1	S_1	Nil	0·4	0·75
2	S_2	Nil	0·03	>3·6
3	$S_1 + Cl_1$	Nil	Nil	Nil
4	$S_2 + Cl_1$	Nil	Nil	<0·14
9	$S_1 + P_1$	Nil	0·26	0·1
10	$S_1 + P_2$	Nil	Nil	<0·05
11	$S_2 + P_1$	Nil	0·2	Almost nil
12	$S_2 + P_2$	Nil	(Nil)	Nil

Section 3—Phosphorus-Bearing Films

Blend No.	Additive(s)	Film thickness (mg P^{32}/sq cm)		
		At 100° C	At 150° C	At 200° C
5	P_1	Nil	Nil	<0·006
6	P_2	0·04 *	0·06	0·06
13	$S_1 + P_1 + Cl_1$	Nil	0·01	<0·01
14	$S_1 + P_2 + Cl_1$	0·4 *	(0·3) *	1·0 *
15	$S_2 + P_1 + Cl_1$	Nil	Nil	0·18
16	$S_2 + P_2 + Cl_1$	0·2 *	0·2 *	0·4 *

Section 4—Sulphur-Bearing Films

Blend No.	Additive(s)	Film thickness (mg S^{35}/sq cm)		
		At 100° C	At 150° C	At 200° C
1	S_1	Nil	0·4	0·75
2	S_2	Nil	0·03	>3·6
13	$S_1 + P_1 + Cl_1$	Nil	<0·1	<0·1
15	$S_2 + P_1 + Cl_1$	Nil	Nil	0·21
14	$S_1 + P_2 + Cl_1$	Nil	Nil	<0·1
16	$S_2 + P_2 + Cl_1$	Nil	Nil	>3·6

From the above table certain facts were apparent. These may be stated as follows:

Section 1

1. The active phosphorus compound attacked the metal at all three temperatures, whilst the tricresyl phosphate had no action below 200° C. Even at this temperature the metal was attacked only to a small extent.

2. Attack by the tricresyl phosphate was not promoted by any of the chlorine or sulphur-bearing compounds studied.

3. Attack by the active phosphorus compound was not significantly decreased by the presence of the other compounds studied, but was materially increased at 200° C by both chlorine and sulphur compounds.

Section 2

1. Attack by sulphur increased markedly with temperature, and the same was true of dibenzyl disulphide.

2. The active phosphorus compound and the chlorinated compound reduced the attack due to combined and free sulphur very materially at the higher temperatures.

3. Tricresyl phosphate appeared to promote attack by dibenzyl disulphide at 150° C, but to inhibit it at 200° C.

Section 3

1. The action of tricresyl phosphate on steel was little affected by the presence of the other compounds except in the case of blend No. 15, where there was a surprising increase in activity at 200° C.

2. The presence of both sulphur and chlorine promoted attack at all temperatures by the active phosphorus compound.

Section 4

1. The formation of a sulphur-bearing film from sulphur was materially reduced in the presence of combined phosphorus and chlorine compounds.

2. Attack by dibenzyl disulphide was also materially reduced in every case except with blend No. 16 at 200° C.

In view of the importance of the above conclusions some further work was done to determine:

(*a*) if a sulphur-bearing film could be replaced by chlorine from an oil solution of the chlorinated compound;

(*b*) if a chlorine-bearing film could be replaced by a phosphorus-bearing film in the same way.

Using disks pre-coated with either a sulphur or chlorine-bearing film, the level of radioactivity at the surface of the disks was measured from time to time with the following results:

(*a*) At all three temperatures studied (100° C, 150° C, and 200° C) there was continuous removal of sulphur-bearing film, reaching a steady state at about 30 per cent removal.

(*b*) Phosphorus in the active phosphorus compound vigorously displaced the chlorine-bearing film. Phosphorus in tricresyl phosphate failed to displace the chlorine-bearing film at 100° C and 150° C, and only succeeded to a very limited extent at 200° C.

Actually, it proved quite easy to determine visually the nature of the film on the surface. The sulphur-bearing film, probably iron sulphide, was blackish in appearance; the phosphorus-bearing film, probably a phosphide, was dark grey; and the chlorine-bearing film was a light reddish brown.

DISCUSSION

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when hypoid gears are operated under high-speed high-load conditions than under low-speed high-torque conditions. Evans and Tourret [28] investigated the pitting of bronze disks under simulated worm-gear conditions and concluded that pitting was initiated by surface or internal cracks, the former being caused by fluctuating compressive and tensile stresses. The rate of pitting could be increased by using certain EP lubricants containing sulphur or sulphur and chlorine.

Failure of hypoid gears under low-speed high-torque operating conditions is due to rippling, ridging, or pitting, which may be regarded as three stages of surface distress associated with the working of the surfaces. The suggestion is therefore put forward that with FS-VVL-761 type oils local temperatures under low-speed high-torque operating conditions are sufficiently high for a ferrous chloride film to be formed, but not high enough to raise it above its melting point. An adherent film of high shear strength is therefore present on the gear teeth which does not prevent the cold working of the surfaces. As the speed increases, however, local temperatures increase also, the film melts, and satisfactory EP lubrication is achieved.

In the presence of an active phosphorus compound, such as the one the authors have examined, a phosphorus-bearing film is formed preferentially. This, probably a phosphide, is a soft grey material readily rubbed off and appears therefore to have low shear strength even in the solid state. Since this is formed at quite low temperatures, it is understandable that satisfactory lubrication is obtained under low-speed high-torque conditions as in the modified SAE machine test. As local temperatures increase, chloride and even sulphide films may be produced from mixtures of the three types of additive as evidenced in Table XIV, Section 4 (200° C). When a relatively inactive phosphorus compound, such as tricresyl phosphate, is used, the ferrous chloride film is formed preferentially and no benefit accrues under low-speed high-torque conditions.

Confirmation of this theory was provided by the fact that certain oil compositions containing both the active phosphorus compound and compounds containing highly reactive chlorine-bearing impurities gave high wear in modified SAE machine tests. It would seem that in these cases there was competition for the surface between the chlorine and the phosphorus, the formation of a uniform phosphide film being thereby prevented.

Certain zinc dialkyl dithiophosphates have also been used successfully in conjunction with sulphur and chlorine compounds to provide EP lubrication under low-speed high-torque conditions. These probably function in a similar manner to the active phosphorus compound. In this connexion, Vinogradov and coworkers [29-30] have shown, in experiments with tributyl trithiophosphite and related compounds, that phosphorus reacts predominantly with steel at all temperatures, phosphide films being formed in preference to sulphide films.

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DISCUSSION

A. Towle: In spite of the fact that I, as a test engineer responsible for the full-scale axle tests carried out by my company, could possibly look forward to a period of reduced activity should the authors' efforts to predict axle test performance be too successful, there is no doubt that we should all heartily welcome any efforts to simplify the problem of gear lubricant development by means of relatively uncomplicated bench tests.

The data presented by the authors derived from bench test EP machines is therefore most interesting and represents a real step in the direction of improving correlation between laboratory bench tests and full-scale axle testing.

From the work carried out by our laboratories, however, as well as the authors' data, it would appear that considerably more work needs to be done before one can rely too heavily on such bench tests, and we believe that for a long time the chief application of bench tests will be in preliminary investigation of new materials, rather than in connexion with specification testing.

Work we have carried out on the Shell four-ball, Timken, SAE, and IAE machines, using different types of gear oil additives, has shown how difficult it is to correlate significance of bench test results when comparing with results from full-scale axle testing.

The procedures used, however, were obviously different from those employed by the authors, so the data would not be directly applicable to the material in the paper.

However, some idea of the heartbreaks possible in attempting correlation tests can be judged from the fact that on ten axle oils run on the IAE gear rig under 4000 rev/min conditions, the first nine lined up extremely well with the known service performance of the oils under high-speed passenger car operation, but the tenth, an experimental blend, had the highest scuffing load of all the oils on the IAE rig, but failed miserably both on the L-19 test and on service trials on passenger cars. The IAE rig is, of course, of the spur gear type, where there is comparatively little sliding, and perhaps for this reason would not be expected to correlate with hypoid conditions where there is high sliding.

Niemann manufactures special gears for hypoid oil testing of his spur gear rig, which is basically the same pattern as the IAE, with the tooth profile modified to increase the slide ratio. As yet, we have had no opportunity to carry out a correlation programme using hypoid oils of known service performance on this rig, but hope to commence one in the near future.

It is believed, however, that, as on the IAE rig, one of the difficulties is to produce failures of the scuffing type at a load which does not give rise to pitting fatigue. On both these machines, however, the cost of carrying out tests is not significantly less than that of a full-scale axle test.

The data developed with radioactive trace techniques are indeed very interesting, and represent a valuable contribution to the study of the mechanisms for the action of EP agents. It would perhaps be more realistic to develop such information under dynamic rather than static conditions. For example, Twiss, Loeser, and Wiquist, in their SAE paper, have shown eight times more phosphorus than sulphur in a film under dynamic conditions with zinc dialkyl dithiophosphate at a bulk temperature of 200° F. Under static conditions at 300° F, the ratio of phosphorus to sulphur was 3 : 6. Up to 250° F under static conditions, the phosphorus was 40 per cent less than the sulphur.

I am inclined to agree with the authors that there is no desperate requirement from the British passenger car industry for oils of better high-speed performance than those now available, although some commercial vehicle manufacturers would probably welcome oils having better high-torque performance. It is significant also that the only two manufacturers of passenger cars who require special factory fill oils are those who do not phosphate-treat their gears.

I cannot let the authors' comments on the Vanguard axle tests go by without challenge. Their statement that these tests were abandoned due to inability to discriminate between oils of satisfactory and unsatisfactory performance is quite untrue.

The Vanguard axle tests are in fact very much alive, and the Full-Scale Axle Working Group of the Mechanical Tests of Lubricants Panel is actively engaged in developing a standardized test technique. True, an untimely delivery of sub-standard gears, believed to have incorrect carbon gradient, did influence the first series of co-operative tests, but this difficulty is now believed to have been overcome by the adoption of gas carburizing by the manufacturers in place of the previous box carburizing.

Deliveries of unsatisfactory batches of gears have, of course, not been unknown in the U.S.A. and a recommendation of the CRC is that check tests on known reference oils should be carried out at prescribed intervals. However, the Americans had sufficient faith in the test techniques they had developed to persevere with them, and did not suggest that the technique was wrong because of setbacks like these.

There is, we believe, a good chance of a suitable high-torque procedure using the Vanguard axle being standardized in the near future.

On the high-speed side, the Vanguard tests have been somewhat complicated by alterations to the run-in techniques which have crept into the procedure as a result of suggestions by various laboratories. In our view, the most critical part of the test procedure is the run-in, and quite minor modifications to the procedure here make significant differences to the test results. There is in fact ample evidence available to indicate that the activity required of the oil once the run-in has been completed can be considerably less than that required for, say, the first 500 miles.

Finally, in attempting to devise a bench test to correlate with the full-scale axle tests it must be borne in mind that the order in which oils rate on these latter tests can be very much modified by merely altering the bulk oil temperature at which the tests are carried out, particularly under high-torque conditions.

J. S. Elliott: Mr Towle's comments are very interesting. Frankly, I expected him to be somewhat more critical than he has been of our attempts to correlate small laboratory EP testing machines with axle tests. Certainly the work described in our paper must be regarded only as a preliminary exploration of the possibilities, and a great deal more remains to be done.

On the question of the economics of testing hypoid gear oils, the small EP machines possess a great advantage over larger machines, such as the IAE gear machine.

I must apologize for the statement about the Vanguard axle. I was not aware of the real reason for this test having been dropped from the latest British specification.

S. G. Rushton: First of all, I should like to congratulate the authors on producing rippling in the SAE machine. I think the production of this phenomenon on a

small scale on a laboratory machine will help us to understand it much more fully.

I should like to comment mainly on the use of the four-ball machine to predict the performance of hypoid oils, under high-speed conditions, in the rear axle of a vehicle. We have made an attempt to find some correlation between the performance of a series of 19 hypoid oils, in the four-ball machine and in the rear axle of a car under conditions of impact loading at high speeds. This test was somewhat similar to the L-42 test described in the paper. The axle test showed that we could divide our series of 19 oils into two groups, a group giving light scuffing in the test, and a group giving heavy scuffing. We did not find it possible to place the same oils in these two performance groups on the basis of the following criteria in the four-ball machine. (1) Shape of the wear–load diagram. This rather is a nebulous criterion, but those who have dealt with wear–load diagrams know that one needs something of the aptitude of a phrenologist to study these things. (2) 2½-second seizure delay load. (3) Mean Hertz load. (4) Weld load. In particular, in this series of tests we found that the oil with the highest resistance to scuffing had the lowest value of 2½-second seizure delay load, and the lowest value of mean Hertz load, whereas we might have expected exactly the opposite. This particular oil contained sulphur alone in the EP additive. The results in this series of tests led us to believe that the question of the additive type, and in particular the balance between the activity of the sulphur and the chlorine in the additive, might affect the correlation. We were also concerned about the very large difference between the sliding speed in the four-ball machine, which is about 120 feet a minute, and in the hypoid axle, which at high speeds can be well over 1000 ft/min. We decided to test hypoid oils containing various concentrations of two EP additives, one a sulphur-chlorine type, and the other containing sulphur alone. In order to take account of the large difference in sliding speeds, we modified the four-ball machine to run at 4000 rev/min, as well as at the standard speed of 1500 rev/min. These results show that no further correlation existed between the two test methods, the four-ball machine and the axle test, with the same criteria as before, either at the standard speeds of 1500 rev/min, or at the increased speed of 4000 rev/min.

The axle tests in the car showed that the two additives, the sulphur and the sulphur–chlorine types, were equally effective in preventing scuffing. The performance in the axle test depended almost entirely on the total amount of EP additive, increased concentrations giving improved resistance to scuffing.

However, results in the four-ball test showed that, in both cases, increased concentration of the sulphur–chlorine additive gave a reduction in wear on the wear–load diagram, while an increased concentration of the sulphur additive gave an increase in wear. These results tend to contradict the ideas set forward in the paper that a minimum load for a given amount of wear might be a useful criterion to predict the performance of hypoid oils from four-ball tests.

I think that before we can use the four-ball machine for the prediction of performance we have to know a lot more about the effect of some of the operating factors involved. For instance, the four-ball test is qualitatively different from a test in an axle, in that in the four-ball machine the wear scars on the three lower balls are continuously rubbed—there is no intermittent sliding—whereas in the hypoid gear both surfaces are going into and out of contact all the time.

The relative radius of curvature in the four-ball machine is very small, compared with that in the hypoid gear. The effect of initial surface finish on the relative performance of different types of EP additives might well make a big difference. I think the surface finish of the balls used in the four-ball machine is about ½ to 1 micro inches, whereas it is much rougher in hypoid gears. Some work in the SAE machine on the effect of surface finish on the relative performance of EP additives showed that a rougher initial surface finish tends to help the sulphur-containing additive against one containing both sulphur and chlorine.

The effect of sliding speed, which I mentioned earlier, could also have a fairly big effect on the relative performance of EP additives. It is, of course, mentioned in the paper that the phosphorus type of additive tends to be much more effective at the lower than at the higher speed.

So our feeling would be that although the four-ball machine is very useful for the fundamental work, our present level of knowledge is not yet sufficient to enable us to predict the performance of hypoid oils in full-scale axle tests.

J. S. Elliott: Mr Rushton has made some very interesting comments. First of all, the rippling on the surface of the test cups will be evident from the specimens.

Secondly, concerning the use of the four-ball machine with different types of additives, the additives examined in our paper have all been of the sulphur–chlorine or the sulphur–chlorine–phosphorus type. We have not examined on the four-ball machine, in this connexion, a material which would give a sulphide film. I think we have to bear in mind that a chloride film or a chloride and phosphide film is produced by this type of additive combination. If a sulphide film is laid down, quite a different set of conditions obtains and the criteria we have suggested may not apply.

We have noticed that, with compositions containing active sulphur, the wear–load curves tend to be much flatter and seizure takes place at much lower loads than with compositions of the sulphur–chlorine–phosphorus type.

We quite agree that there is much work yet to be done on the effect of variations in sliding speed and other conditions, and hope that we shall have the opportunity of doing some as time goes on.

P. Jenner: I would like to ask the authors for a few practical details about the determination of these two new proposed criteria on the four-ball machine.

I think I am right in saying that the determination of 1 mm wear load, and also the load–wear increase, relies largely upon an accurate drawing of the centre limb of the graph. When we are normally drawing a wear–load diagram, it is the practice to construct the centre limb of the graph by joining the last point of no seizure to the first point of immediate seizure. The points due to delayed seizure are then presented as a scatter around this centre line. The authors, in drawing their graphs, have in many cases shown a step over this delayed seizure range. We find that, on repeated tests, scatter is quite considerable in this delayed seizure range, and I would be interested to know exactly how many tests it is necessary to do before one could accurately draw in this centre limb of the graph, because the slope of that line will entirely govern accuracy of the results.

E. D. Edwards: I do not really know the answer as to how many points one needs to determine, but it seems to us, in our experience so far, that we can determine the " 1 mm load " fairly precisely, *i.e.* we can, over a fairly nar-

row range of loads, obtain this big step in the curve. It will be noticed in the paper that there are fairly big distinctions made by our standards between oils which are satisfactory and those which are unsatisfactory. We fully admit, as Mr Elliott has already said, that we require to do a lot more work before establishing this criterion. It seemed to us, though, that it distinguished between the oils known to pass the high-speed test and those known to fail it, so it was put forward for discussion.

In this narrow range we have not made statistical determinations of the precision, and further work definitely needs to be done, so I am afraid I cannot completely answer the question. But I do not think there is perhaps such a wide scatter of results as Mr Jenner fears. For one thing, the slope that we take is chosen over a range of 20 kilos; very often the step in the graph is less than that, which tends to cover up the errors.

P. Jenner: As further comment, I would draw your attention to a criterion that was proposed some time ago, the Pressure Wear Index, which also relied upon the slope of the centre limb of the graph, and I think that was largely dropped from favour because of the difficulty in determining precisely the top and the bottom turning points of the graph. Apart from that, to justify the drawing of a step in the middle, through a scatter of points, I feel one would have to repeat the test a number of times, and a reliable result would be rather difficult to determine, unless carried out statistically.

A. Watson: I am rather interested in the data for correlation of axle tests, because the axle is realistically a part of a vehicle and I should have thought that the first thing to be checked would have been some method of assessing the temperature of the rubbing contact. We all know from the axle test rigs that the rise of the bulk oil temperature varies at different times with different oils and under different conditions. Could the authors of the paper say if any work has been done on the determination of the maximum rubbing contact temperature?

Secondly, we do know that axle conditions in America are more critical than in the U.K. The reason for using the Dodge axle in the first place in these tests, I believe, as stated in America in 1950, was mainly because it had the greatest offset angle of any hypoid known. I imagine that is still one of the critical things. Can the authors say, for example, taking samples from our used analysis of oils in axle sumps, if there is any indication that we do not get such high temperatures at rubbing contacts as the Americans? Alternatively, can they say that we do get lower temperatures? Has any work been done on this?

J. S. Elliott: I am afraid that we have no information on maximum rubbing contact temperatures. We have taken into account the bulk oil temperatures that are employed in the L-42 and L-37 tests, which we assume have been chosen on the basis of service experience in America. As to the difference between the temperatures reached in the U.K. and those reached in America, I am afraid I cannot say anything. The fact that there seems little interest at present, on the part of British car manufacturers, in oils of better high-speed performance, may indicate, however, that we do not get such high temperatures as in the U.S.A.

A vote of thanks to the authors was accorded with acclamation.

CONTRIBUTED DISCUSSION

A. W. Pottier: I have been carrying out some work on the four-ball machine and have concentrated so far on the mean Hertz loads. The emphasis on the wear–load curves and " 1 mm load " scar diameter is particularly interesting.

Am I correct in assuming that this " 1 mm load " scar is measured after a one-minute run?

One criticism of the four-ball machine is that a temperature measurement is not possible. Have the authors found that temperature alone has influenced the results, say on the SAE machine, because in Tables X and XI the load and the temperature have been increased?

If the load had remained at 200 lb and the temperature raised to 275° F, would different results have been obtained?

In the determination of the mean Hertz load the viscosity of the base oil has been found to influence the results in direct ratio with viscosity increase, *i.e.* the mean Hertz load increased with rise in viscosity. Have the authors experienced a similar trend?

J. S. Elliott: Mr Pottier is correct in assuming that the " 1 mm load " scar is measured after a one-minute run.

With regard to the effect on temperature, I am afraid we have not had the opportunity to investigate on the SAE machine the effect of increasing temperature and load independently of one another as Mr Pottier suggests. This is because we were concentrating upon trying to correlate with the L-20 and L-37 tests respectively. It would be interesting to investigate this some time. I think it is quite probable that we should have obtained different results. One point that has become apparent is that certain additives have a critical decomposition temperature between 225° and 275° F and are, therefore, not suitable for use at the higher temperatures.

There is a modification of the four-ball machine known as the four-ball wear testing machine, which can be operated at different temperatures.

We are unable to make any definite statement about the effect of viscosity on four-ball test results, since we have concentrated on SAE 90 oils in our work. We believe that it is generally true, however, that increasing viscosity results in improved load-carrying capacity, and some years ago we noticed this trend in work on the SAE machine.

MEASUREMENT OF STRATA DIP: THE BEAMED CURRENT DIPMETER *

By P. THREADGOLD † (Associate Fellow)

1. INTRODUCTION

THE difference in specific gravity between oil or gas and underground water causes the hydrocarbons to migrate through permeable rocks in an upward direction. The migration will continue until the hydrocarbons encounter an impermeable barrier against which they will accumulate.

When wildcat exploration boreholes are drilled, porous rocks are frequently encountered in which there are traces of hydrocarbons. This indicates a potential reservoir rock through which hydrocarbons may have migrated. In such cases it is essential to know the direction and angle of inclination of the impermeable layer or cap rock above the reservoir, in order that future boreholes may be located updip from the first.

If hydrocarbon accumulations are encountered, their extent must be evaluated as quickly and economically as possible. An accurate knowledge of the angle and direction of inclination of the top and bottom of the reservoir rock in all evaluation wells subsequently drilled speeds the initial estimation considerably.

Two methods of measurement of the angle and azimuth of strata dip are in current use:

(*a*) Direct measurement on cores which have been oriented by locating marks prior to cutting the core (*e.g.* the Eastman Corex Method).

(*b*) The recording of dipmeter logs over a given section of the borehole, using some form of three-probe logging device.[1–3]

The use of oriented cores can give extremely accurate results. The method is, however, time-consuming, costly, and not always convenient to use. In addition there is little guarantee that the dip measured from a core, however accurate, is representative of the angle of dip required. Unless the core is taken through a stratigraphical interface, only the angle of the deposition of the bed will be measured. This is not necessarily the same as the angle of dip of the top and bottom boundaries of the bed.

Measurement of strata dip angles by a logging tool which can be lowered into the borehole is a more practical proposition. In a relatively short period dipmeter logs can be run over any number of desired levels in the open hole. The levels can be chosen with due regard to all other information previously collected, *e.g.* cuttings logs, electrical formation logs, etc.

The dipmeter log is widely used in oilfield exploration and exploitation drilling. The accuracy of the results obtained, especially when the angle of strata dip is small, is, however, questionable. It is generally accepted that where the angle of dip is less than 5° the dipmeter results are not valid. The following paragraphs discuss the principle of dipmeter logging tools, and the factors affecting the accuracy of the measurements made. A new type of dipmeter using a focused current beam designed to minimize the errors in dipmeter logging is described.

2. PRINCIPLE OF DIPMETER LOGGING

Conventional dipmeter tools consist of three spring arms which press some form of probe system (usually electrodes) against the borehole wall. The probes are spaced 120° apart round the axis of the tool, and measure some formation characteristic (usually electrical resistivity). The signal from each probe system is transmitted to surface along the logging

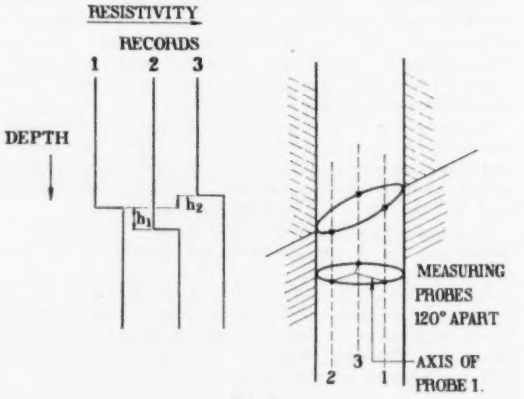

FIG 1

PRINCIPLE OF THREE-PROBE TYPE DIPMETERS

cable, which serves to raise and lower the tool in the borehole. At surface, each probe signal is recorded continuously against depth in the hole. As each probe crosses a change in stratigraphy this will be indicated by a change in the surface record. If the boundary plane crossed is not perpendicular to the

* MS received 1 April 1959.

† The British Petroleum Co. Ltd.

borehole axis each of the probes will cross it at a different depth. Measurement of these depth differences and knowledge of the diameter of the borehole enable the angle of the plane containing the intersection of the interface with the paths of the three probes to be calculated with respect to the plane of the probes.

Auxiliary means are provided for orienting the three probes with respect to vertical and to magnetic north. The calculated angle of the stratigraphical interface can then be referred to these two directions.

The method is illustrated in Fig 1.

3. FACTORS AFFECTING THE ACCURACY OF THREE-POINT DIPMETER MEASUREMENTS

(a) *Resolution of the Instrument at a Finite Stratigraphical Interface—Depth of Investigation*

The resolution of any three-probe electrode system at a finite stratigraphical interface is a function of the electrical length of each probe and its radial depth of investigation into the strata surrounding the well bore. Consider the theoretical example shown in Fig 2, where each probe is considered to have an

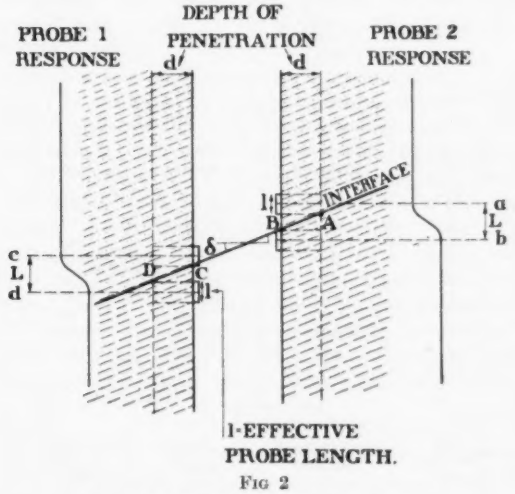

FIG 2

FACTORS AFFECTING DIPMETER ACCURACY

electrical length l and a depth of investigation d; probes 1 and 2 are shown for convenience looking down- and updip respectively. The depths of the probes are measured to their mid-points.

As the probes pass from above the interface $ABCD$ through and below it, probe 1 will begin to indicate a change in stratigraphy when the bottom of the probe is at point C and cease to indicate it when the top of the probe is at point D. Similarly, probe 2 will indicate the change as occurring from half the probe length above A to half the probe length below B. The total depth L over which the change will be indicated by one probe is therefore equal to $(l + d \tan \delta \cos \psi)$, where δ is the true angle of dip of the interface and ψ is the angle between the axis of the probe considered and azimuth of dip. (In Fig 2, $\psi = 0$, hence $L = l + d \tan \delta$.) This leads to the commonsense result that the sharpest indication will be given by a probe looking along the line of zero slope of the interface (*i.e.* $\psi = 90°$, hence $L = l$).

Again considering the limiting case shown in Fig 2, where two probes are considered, one (probe 2) with its axis facing updip and the other (probe 1) with its axis facing downdip; it will be noted that apparently correlating points on the records are not in fact correlatable. For probe 1 response, the correct point of intersection of the interface with the well bore (point C) is $l/2$ below the top of the indication of change on the record (point c), while for probe 2 response, the correct point of intersection (point B) is $l/2 + d \tan \delta$ below the top of the indication of change on the record (point a). Alternatively, the correct correlating points on the probe records are $l/2$ *above*, the lower indication (point b) for the probe 2 (and for all probes having an *up*dip component along their axes), and $l/2$ *below* the upper indication (point c) for probe 1 (and for all probes having a downdip component along their axes). It is clear that a completely correct correlation of the dipmeter probe records is possible only when the direction of dip is known. Unfortunately, this is one of the unknowns that the dipmeter is intended to determine. Straightforward correlation of the dipmeter records can lead therefore to errors in the depth differences h_1 and h_2 (Fig 1) having a magnitude of up to $d \tan \delta$.

TABLE I

Examples of Mean Error $d\psi$ *in Azimuth* ψ *in an 8-inch Borehole as a Function of the Angle of Dip* δ *and the Measurement Error* dh *in* h_1 *and* h_2

Observed angle of dip, δ	dh, in.	Error $d\psi$, in azimuth for various values of ψ			
		$\psi = 0°$	$\psi = 30°$	$\psi = 60°$	$\psi = 90°$
2°	0·05	39·5°	20°	42°	13·0°
	0·10	59°	35°	87·5°	25·5°
	0·15	68°	45°	110°	35·5°
	0·20	73°	60°	114·5°	43·5°
	0·25	76·5°	66°	118°	50·0°
5°	0·05	10°	9°	6°	55°
	0·10	19°	18·5°	5·5°	5·0°
	0·15	27°	24·5°	20·5°	16·0°
	0·20	34°	32·0°	27·5°	20·5°
	0·25	41°	39·0°	42·0°	25·5°
10°	0·05	5°	4°	2·5°	2·5°
	0·10	9·5°	8·5°	5·5°	5·0°
	0·15	14·0°	11·5°	8·5°	7·5°
	0·20	18·0°	16·0°	11·0°	10·0°
15°	0·05	3°	Negligible		
	0·10	6°			
	0·15	9°			

TABLE II

Error Δ in δ for Various Values of dh *and δ (for an 8-inch Borehole)*

Maximum Δ for given δ occurs at $\phi = 90°$ or 270°.
Mean Δ for given δ is the mean of maximum and minimum Δ over the range of ϕ0°–360°.

δ°	dh = 0·05 in.		dh = 0·1 in.		dh = 0·15 in.		dh = 0·2 in.		dh = 0·25 in.	
	Max Δ°	Mean Δ°	Max Δ°	Mean Δ°	Max Δ°	Mean Δ°	Max Δ°	Mean Δ°	Max Δ°	Mean Δ°
1	0·8	0·6	1·7	1·4	2·5	2·1	3·3	2·9	4·2	3·7
5	0·7	0·55	1·5	1·2	2·3	1·8	3·1	2·5	3·9	3·1
10	0·7	0·55	1·5	1·2	2·2	1·8	2·8	2·4	3·5	3·0
20	0·7	0·55	1·5	1·1	2·2	1·7	2·7	2·2	3·4	2·7
30	0·6	0·4	1·2	0·8	1·7	1·2	2·3	1·6	2·9	2·0
45	0·4	0·4	0·8	0·6	1·2	1·0	1·6	1·2	2·0	1·4
60	0·2	0·1	0·4	0·2	0·6	0·4	0·8	0·55	1·0	0·6
70	Negligible		—	—	—	—	0·3	0·3	0·5	0·5
80	—	—	—	—	—	—	—	—	—	—

δ = Angle of dip.
ϕ = Azimuth of dip relative to electrodes.

The above discussion indicates that the magnitude of the errors in measuring h_1 and h_2 decreases as the angle of dip δ decreases. This, of course, is true, but in the practical case where $\delta \rightarrow 0$ a very small error in measurement of h_1 and h_2 can lead to large errors in the angle of dip and complete ambiguity in the azimuth of dip.

Tables I and II give examples of the errors in the computed angle and azimuth of dip (δ and ϕ respectively) for different values of dh, the measurement error in h_1 and h_2. These results were obtained in the course of the work at the BP Research Centre, Sunbury-on-Thames.

(b) *The Effects Due to Lithology*

It is very rare for any lithological interface to be a sharp boundary, and it is understood that the minimum thickness of transition to be expected between beds is of the order of $\frac{1}{3}$ inch. In many cases, *e.g.* shale/sand sequences, the transition from one stratum to the other can occupy an appreciable thickness. All of these factors add to the indefiniteness of correlation between three dipmeter curves.

In addition, the fact that a natural stratigraphical interface is rarely a true plane should be considered. This is especially true in sedimentary sequences, which are of prime importance to the petroleum geologist. If the local undulations in the various interfaces are comparable in magnitude to the recorded values of h_1 and h_2, obviously the calculated dip is only that of the plane containing the junctions of the interface with the borehole wall along the lines of contact of the three electrical probes. While in this case the dipmeter could be giving a perfectly true representation of the facts, the resulting angles of dip and azimuth might have no relationship to the mean angle and azimuth of dip of the strata. In practice, the log interpreter would probably not attempt an interpretation of a dipmeter log taken over such a sequence. Table III shows the angle and azimuth of dip computed over four geological interfaces, from ten separate records taken with different dipmeter instrument orientations. The variations round each interface as the instrument orientation changes are shown to be exceptionally large. The logs were taken over a sand/shale sequence in the Millstone Grit

TABLE III

Variation in Computed Angle and Azimuth of Strata Dip for Various Dipmeter Orientations

All azimuths quoted relative to magnetic North

(a) *Interface* 1

Run No.	Instrument azimuth	Dip angle	Dip azimuth
2	287°	2° 51′	129°
3	270°	4° 36′	64°
4	235°	4° 54′	161°
5	212°	3° 9′	90°
6	190°	5° 42′	305°
7	170°	4° 3′	142°
8	12°	1° 54′	109°
9	285°	3° 36′	174°
10	260°	3° 12′	107°

(b) *Interface* 2

Run No.	Instrument azimuth	Dip angle	Dip azimuth
2	287°	2° 54′	95°
3	270°	2°	50°
4	235°	2°	165°
5	212°	1°	212°
6	190°	1° 30′	260°
7	170°	3° 30′	268°
8	12°	4°	110°
9	285°	2° 30′	205°
10	260°	4°	109°

(c) *Interface* 3

Run No.	Instrument azimuth	Dip angle	Dip azimuth
2	287°	3½°	104°
3	270°	11° 18′	70°
4	235°	2° 3′	161°
5	212°	6°	129°
6	190°	12°	50°
7	170°	16°	357°
8	12°	7° 24′	19°
9	285°	70°	92°
10	260°	9° 32′	82°

(d) *Interface* 4

Run No.	Instrument azimuth	Dip angle	Dip azimuth
1	248°	10°	117°
2	287°	3° 33′	113°
3	270°	1° 6′	105°
4	235°	3° 33′	204°
5	212°	6° 15′	179°
6	190°	6° 18′	196°
7	170°	5° 45′	144°
8	12°	5° 9′	166°
9	285°	3° 27′	118°
10	260°	8° 12′	115°

Series in Nottinghamshire, U.K., in an area where considerable minor faulting is believed to have taken place. The results were not therefore entirely unexpected, but serve to show the unreliability of only one or two three-probe dipmeter records taken over a given interval.

4. DESIGN AND TESTING OF A BEAMED CURRENT DIPMETER *

(a) *Requirements for a Practical Field Dipmeter*

Consideration of the various sources of error in dipmeter surveys leads to the general specification of a practical dipmeter giving high accuracy in definition of stratigraphical interfaces. This again falls into two categories: first, the requirements for an instrument to give accurate representation of the facts, and secondly, the method of using the instrument in order to obtain sufficient information to compute the angle and azimuth of mean geological dip to the accuracy required.

(i) *Instrumental Requirements.* Any dipmeter giving a true representation of the conditions down the hole must be designed in such a way that the various errors discussed in Section 3 (*a*) are kept to a minimum. This means simply that the electrical length and depth of investigation of the probe systems must be kept to a minimum.

(ii) *Selection and Presentation of Basic Data.* If it could be assumed that the stratigraphical interfaces over a given section of a borehole were planar and that each interface was uniform round the complete circumference of the well bore, a single run with three probes 120° apart would suffice to identify the dip plane. However, the more the interfaces round the circumference of the well depart from true planes, the more runs will be required at different probe orientations. In addition, should there be any anomalous interfaces in the section surveyed due to current bedding, faulting, etc., the methods of display and interpretation must enable their occurrence to be recognized.

(b) *Realization of an Accurate Field Dipmeter Instrument*

A dipmeter has been designed in the Exploration Division of the BP Research Centre which approaches the ideal required for instrumental accuracy.

The instrument works on the focused current principle and has no contact with the borehole wall. The investigating probes are three current beams, originating at circular electrodes, $\frac{1}{3}$ inch in diameter, located 120° apart round the body of the sonde and insulated from it. The operating section of the sonde body acts as potential guard electrode, being 2 feet long. Alternating current is fed via the logging cable from surface to the guard, and thence to each probe electrode by three very low impedance primary windings of the signal transformers. The low impedance of the primary windings and the relatively small current emitted by each probe electrode results in the guard and probe electrode potentials being substantially equal. This ensures

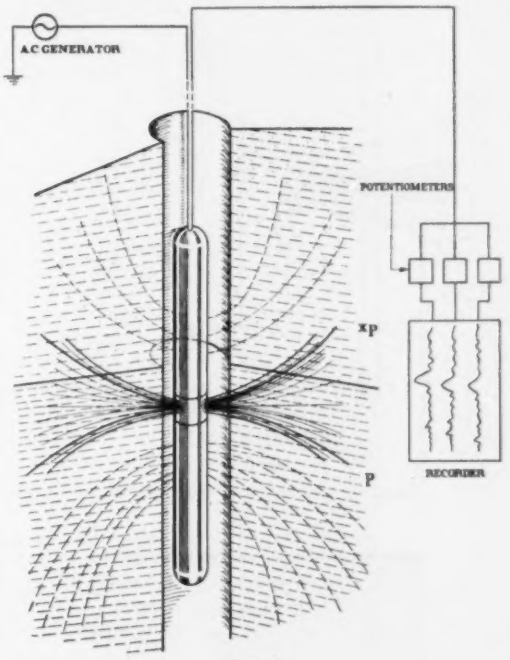

FIG 3
THE BEAMED CURRENT DIPMETER

that the current from each probe electrode leaves the surface normally in the form of a pencil beam.[4] In practice, the small potential drop across the primary of the signal transformer has been compensated by the provision of auxiliary guard ring electrodes fed with current from the main guard body through a resistance. The resistance value has been chosen to give a potential drop equal to that occurring across each transformer primary. The change in intensity of current emitted by each probe electrode as the latter crosses a resistivity interface is reflected as a change in potential across the secondary winding of the corresponding signal transformer. The signals are amplified, rectified, and recorded as a log at surface. The relatively short potential guards cause the probe current beam to have an angular divergence in the vertical plane of approximately $1\frac{1}{2}$° in a homogeneous medium (*i.e.* borehole fluid) and of approximately 3° in the horizontal plane. The effect of the relatively resistive borehole wall is to cause

* Patent applied for.

this beam to diverge, and the depth of investigation becomes correspondingly small. Figs 3 and 4 illustrate the general principle of the instrument.

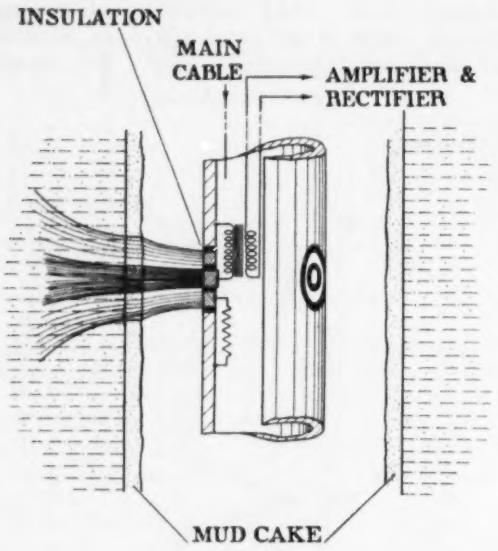

FIG 4

DETAIL OF THE BEAMED CURRENT PROBE

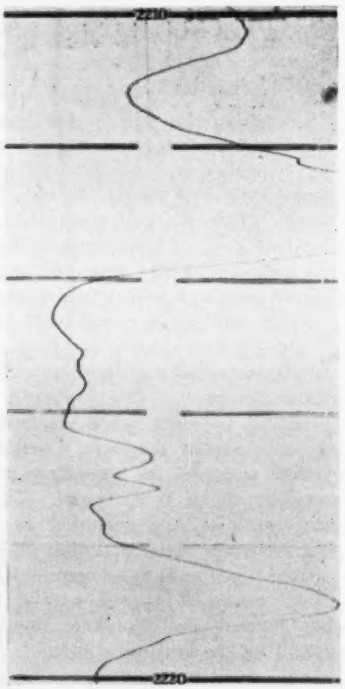

FIG 5

SINGLE PROBE TRACE SHOWING DEFINITION

(c) Field Test Results

Results of initial field tests of repeatability and definition using a single probe electrode are shown in Figs 5 and 6. Fig 7 is a copy of a run taken with the

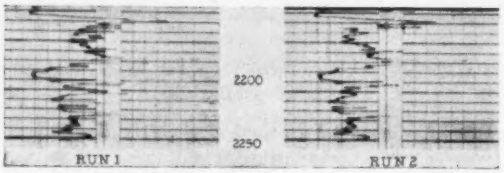

FIG 6

SINGLE PROBE TRACE SHOWING REPEATABILITY

FIG 7

TYPICAL DIPMETER TRACE USING THE BEAMED CURRENT DIPMETER

prototype three-electrode instrument over 14′ of a thinly bedded shale/sand sequence in the U.K. Coal Measures. This shows the fine definition and detail

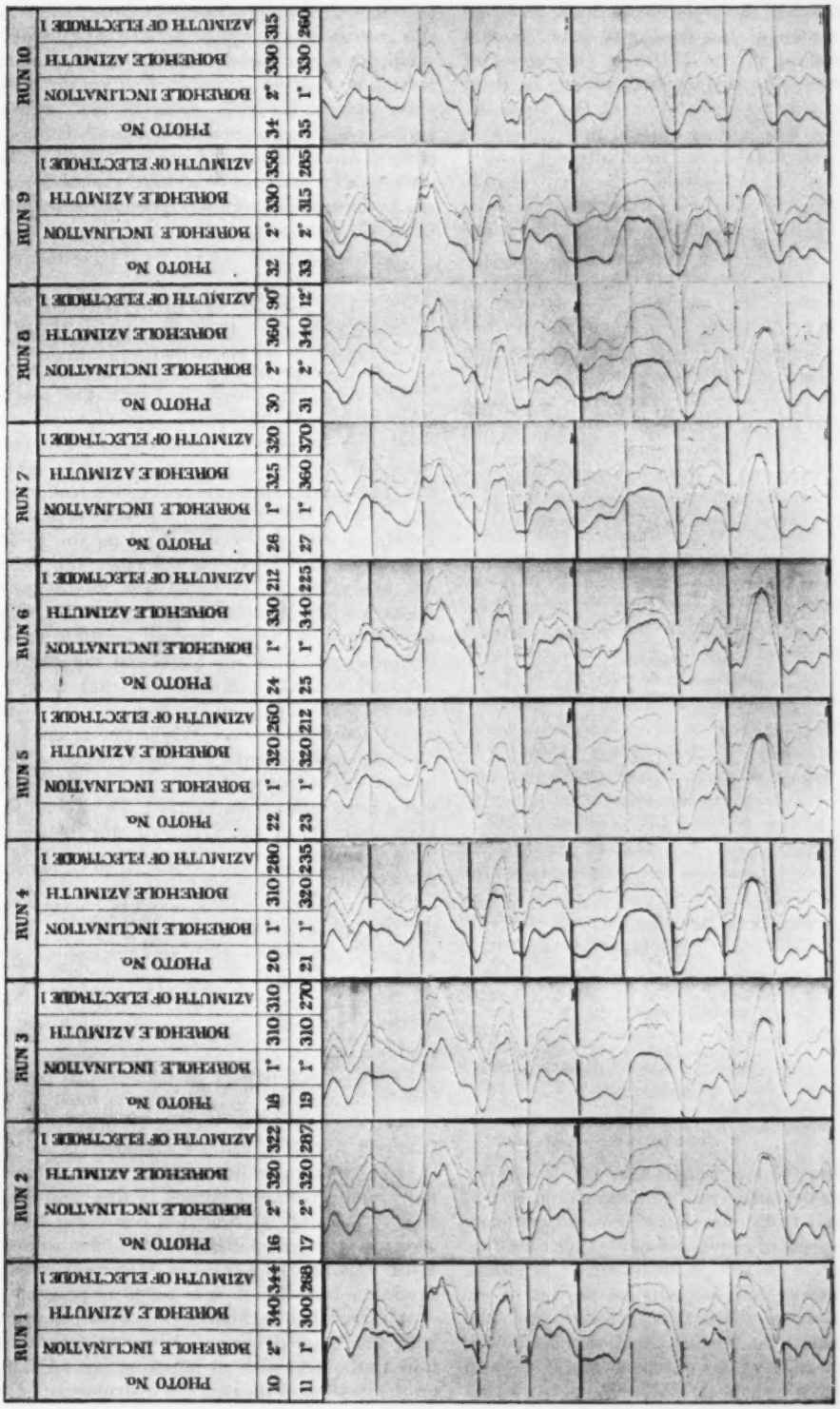

FIG 8
TEN SUCCESSIVE DIPMETER RUNS SHOWING EFFECT OF SONDE ORIENTATION

picked out by each of the probe electrodes. As a final field test, a series of ten runs was taken over a sand/shale interval in the Millstone Grit series of Nottinghamshire. A single shot photoclinometer only was available for orientation of the dipmeter. The instrument was moved up and down the hole prior to each individual record in an attempt to alter the orientation of the sonde. The ten records obtained, together with the relevant orientation data, are shown in Fig 8. Some jitter is evident on various traces due to a slight instrumental fault, but the reproducibility of the various interface indications is well demonstrated. In addition, the change in character of individual interfaces round the circumference of the borehole is apparent from comparison of records taken at different sonde orientations. Table III (*a–d*), previously discussed, gives the angles and azimuths of dip of four specific interfaces, computed for the different sonde orientations.

As could be expected in the sedimentary sequence concerned, the stratigraphical interfaces are far from planar and show little correlation one with the other.

TABLE IV

Mean Dip over Interval 2950 *ft*–2970 *ft*

Run No.	Depth	Borehole inclination	Azimuth of borehole inclination	Instrument azimuth of electrode 1	Formation dip angle	Formation dip azimuth
1	2970	2°	340°	344°	3° 15′	168°
1	2950	1°	300°	248°	2° 18′	110°
2	2970	2°	320°	322°	3° 33′	138°
2	2950	2°	320°	287°	3° 27′	122°
3	2870	1°	310°	310°	3° 21′	107°
3	2950	1°	310°	270°	2° 15′	102°
4	2970	1°	310°	280°	1°	183°
4	2950	1°	320°	235°	1° 36′	96°
5	2970	1°	320°	260°	2° 30′	145°
5	2950	1°	320°	212°	2° 21′	128°
6	2970	1°	330°	225°	1° 33′	185°
6	2950	1°	340°	190°	1° 54′	174°
7	2970	1°	325°	210°	3° 6′	200°
7	2950	1°	360°	170°	3° 45′	153°
8	2970	2°	360°	90°	3° 3′	164°
8	2950	2°	340°	12°	2° 9′	126°
9	2970	2°	330°	358°	3° 42′	156°
9	2950	2°	315°	285°	3° 15′	159°
10	2970	2°	330°	315°	2° 15′	101°
10	2950	1°	330°	260°	1° 33′	108°

Mean dip angle = 2° 25′.
Mean azimuth of dip = 141°.

Table IV lists the mean angle and azimuth of dip computed for each single run by obtaining h_1 and h_2 from an overall curve correlation for the complete interval. Two sets of results are quoted for each run. These correspond to the photoclinometer readings, first, at the bottom, and secondly, at the top of the interval. The mean of the twenty results gave the average inclination and azimuth of formation dip. The maximum angle of dip obtained was 3° 45′ and the minimum 1° 0′; the mean value was 2° 25′, which agreed with that previously obtained from cores by site geologists. It will be noted that even at such a small dip angle, the maximum variation in azimuth is from 96° to 200°, a variation of approximately 50° either side of the mean value of 141°, which again agreed with the geological evidence. The maximum error in measurement of h_1 and h_2 was of the order of 0·10–0·15 inch. It is considered that this represents the best practical accuracy possible using a conventional three-probe type dipmeter.

5. THE FIELD APPLICATION OF THE ACCURATE THREE-PROBE TYPE DIPMETER

Section 3 (*b*) above discussed the inaccuracies inherent in any three-probe type dipmeter measurement due to possible variations in the nature of formation interfaces. It can be readily appreciated that an accurate dipmeter will give a true representation only of the points of intersection of a series of interfaces with the well bore along the three-probe paths. In low dip strata the angle and azimuth of dip computed from these data might bear little relationship to the mean geological dip. The field tests described showed that an accurate estimate of the mean geological dip angle and azimuth could be obtained by taking a series of runs over a given interval, and relying on the fact that the instrument would rotate between. While the beamed current dipmeter has no contact with the walls of the borehole, it was in fact used with upper spring centralizers and a lower rubber centralizer. These tend to follow fixed channels in the well wall, and hence there is little guarantee of any appreciable change in instrument orientation between runs.

The interpretation of a series of surveys taken in low dip strata is difficult and requires an interpreter not only conversant with the instrument but also with the geology of the section surveyed. The interpretation is, of course, rendered more difficult by the occurrence of current or cross-bedding phenomena, etc.

Finally, the dipmeter probe needs to be run very slowly during a survey, 200 ft/hr at most, in order to obtain the full detail on the records. This means that one 20-ft level takes 6 minutes; hence ten runs over one interval will occupy at least an hour and a half; and a complete survey of five 20-ft levels will occupy probably at least ten hours' rig time, when account is taken of associated caliper surveys, etc. While this could be justified in certain instances, it would not be satisfactory as a routine process.

It is clear that the high degree of resolution obtained with the beamed current dipmeter cannot be used fully in the field without imposing certain limitations on the method of running the instrument. The most

serious of these is the necessary increase in rig time required for a survey.

The obvious solution to the problem is to utilize the resolution accuracy of the dipmeter in an instrument which produces the effect of multiple runs at different instrument orientations. This can be achieved by using a series of probe electrodes round the circumference of the dipmeter and commutating the measurement in sequence round the probes.

6. THE RESISTIVITY SCANNER *

A beamed current dipmeter using multiple probe electrodes has been designed in which the measuring

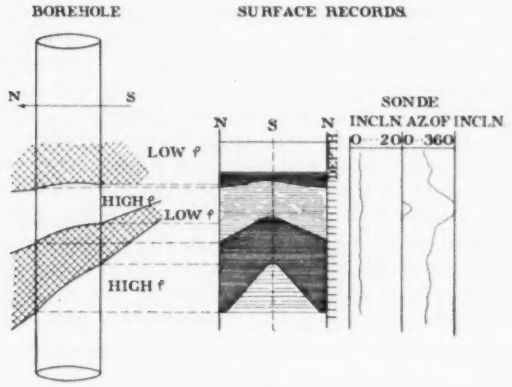

FIG 9

PRINCIPLE OF THE RESISTIVITY SCANNER

circuits are connected in sequence to each of the probe electrodes. The beamed current intensity from each electrode is used to modulate the brightness of the trace of a cathode ray oscilloscope at surface. The trace is triggered as the probe electrode pointing to magnetic north is connected in circuit, and each time base trace corresponds to a scan of 0°–360° round the borehole. The brightness of the trace at any azimuth represents the resistivity of the strata adjacent to the borehole wall at the azimuth indicated. A photographic film passes in front of the oscilloscope in synchronism with the vertical movement of the dipmeter up or down the borehole. An oriented resistivity photograph of the borehole wall will thus be produced, from which strata dip can be measured directly. Fig 9 illustrates the principle described.

7. CONCLUSIONS

The accuracy of results obtained with any three-probe type dipmeter depends first on the stratification conditions in the section of the borehole surveyed. The inherent assumption that the interfaces between successive beds are planar is, of course, incorrect. If the local irregularities in the geological interface are small compared with the mean dip angle the inaccuracies in the angle computed from dipmeter records will also be small.

A second system of errors in dipmeter results arises from the characteristics of the probe system used. The degree of resolution obtained in locating a geological interface depends on the effective probe length, and the radial extent of the measurement into the strata round the borehole wall. Both of these characteristics of the probes need to be as small as possible if a high degree of resolution is to be obtained.

The beamed current dipmeter described has a high degree of resolution at a geological interface, due to its small effective probe length and shallow depth of investigation. In addition, it has the added advantage over conventional dipmeter sondes that the probes are not spring-loaded against the borehole wall. It can therefore be used in slim exploration boreholes where an accurate estimate of strata dip is extremely useful. The centralizers used do not need to be strong springs, but can be soft rubber pads. The consequent danger of the dipmeter sticking in a tight hole is therefore relatively small.

The principle of the beamed current dipmeter has provided the basis for the development of a scanning instrument which will produce at surface a photographic representation of the borehole wall. This resistivity scanner has great possibilities, not the least of which is that it enables strata dips to be measured directly with negligible computation.

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* Patent applied for.

KINETICS OF OIL OXIDATION INHIBITORS *

By K. U. INGOLD †

SUMMARY

The activation energies of a number of elementary reactions that occur in the liquid phase autoxidation of a white mineral oil have been determined. A unified mechanism of inhibitor action is presented.

INTRODUCTION

In recent years considerable advances have been made in measuring the activation energies of the elementary reactions involved in the liquid phase autoxidation of hydrocarbons.[1] As a part of our study on the effects of inhibitors on oil oxidation [2, 3] it was considered of interest to measure the activation energies of some of the elementary reactions involved in the oxidation of the oil that was used in the previous work. Some measurements were also made on the efficiencies of inhibitors at different temperatures.

RESULTS

The apparatus and procedure have been described previously.[2, 3]

Two methods were used to define the induction period of the uninhibited oil. The first definition was the same as that previously used, *i.e.* the time taken by the oil to add 50 per cent of its volume of oxygen at standard temperature and pressure ($t_{0\cdot5}$). The other definition involved plotting the complete oxidation curves and extrapolating the maximum slope back to the point where it cuts the time axis, the intercept being the induction period (t_i). The first method has the advantage of being simpler to obtain and of being applicable over a larger temperature range, since at high temperatures the maximum rate becomes dependent on the rate of solution of the oxygen in the oil. However, the two methods give quite similar induction periods and the temperature coefficients of the induction periods are in good agreement (see Table I). Measurements were also

TABLE I

Activation Energies For Autoxidation and Inhibited Oxidation of White Mineral Oil

Inhibitor	Concn of Inhibitor (g mol/litre)	Temperature Range, ° C	Quantity measured	Activation Energy (kcal/mol)
None		117–172	$(t_{0\cdot5})_{\text{UNINH}}$	−31·0
None		124–151	$(t_i)_{\text{UNINH}}$	−30·9
None		131–151	$(t(P))$	−30·9
None		124–151	$(R_{O_2})_{max}$	20·5
None		131–151	$(R(P))_{max}$	32·0
None		131–161	$(D(P))_{\text{UNINH}}$ extrapolated to zero concentration	31·1
None		131–161	$(D(P))_{\text{UNINH}}$ at 0·20 molar concentration	22·7
N-phenyl-α-naphthylamine	$2\cdot0 \times 10^{-2}$	140–170	$(D(P))_{\text{INH}}$ extrapolated to zero concentration	31·5
α-naphthol	$3\cdot0 \times 10^{-5}$	146–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−41·4
α-naphthol	$6\cdot0 \times 10^{-4}$	179–202	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−36·3
α-naphthol	$6\cdot0 \times 10^{-4}$	179–202	$(t_{0\cdot5})_{\text{INH}}$	−35·9
2,2′ methylene-bis (4-methyl-6-*tert*-butyl phenol)	$5\cdot0 \times 10^{-5}$	154–180	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−42·6
	$3\cdot5 \times 10^{-3}$	180–210	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−37·9
N-phenyl-β-naphthylamine	$3\cdot5 \times 10^{-4}$	130–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−32·8
N-phenyl-β-naphthylamine	$4\cdot0 \times 10^{-3}$	179–202	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−32·6
N-phenyl-β-naphthylamine	$4\cdot0 \times 10^{-3}$	179–202	$(t_{0\cdot5})_{\text{INH}}$	−32·5
Phenol O-*H*	$4\cdot2 \times 10^{-2}$	146–197	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−29·1
Phenol O-*D*	$4\cdot2 \times 10^{-2}$	146–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−28·5
o-Cresol O-*H*	$6\cdot0 \times 10^{-3}$	146–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−32·4
o-Cresol O-*D*	$6\cdot0 \times 10^{-3}$	146–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−31·1
Aniline N-H_2	$3\cdot6 \times 10^{-2}$	134–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−37·8
Aniline N-D_2	$3\cdot6 \times 10^{-2}$	134–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−36·4
N-methylaniline	$1\cdot6 \times 10^{-3}$	146–172	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−34·3
Diphenylamine	$9\cdot0 \times 10^{-4}$	146–178	$(t_{0\cdot5})_{\text{INH}} - (t_{0\cdot5})_{\text{UNINH}}$	−30·3

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made of the temperature coefficient of the maximum rate of oxidation of the uninhibited oil $(R_{O_2})_{max}$.

At the lower temperatures the rate of formation of peroxides was measured by the iodometric procedure of Kokatnur and Jelling.[4] Extrapolation of the maximum rate of peroxide formation $(R(P)_{max})$ to the time axis gave an induction period for peroxide formation $(t(P))$.

The rate of decomposition of the peroxides $(D(P))$ in the absence of oxygen was also measured over a range of temperature both in the presence of an inhibitor (*N*-phenyl-α-naphthylamine at $2{\cdot}0 \times 10^{-2}$ mol/litre [5, 6]) and in its absence. In the presence of the inhibitor the initial concentration of peroxide was $6{\cdot}0 \times 10^{-2}$ mol/litre, but in the absence of the inhibitor the initial concentration used was roughly half the maximum concentration that could be formed in the oil at a temperature in the middle of the range in which the decomposition was studied (0·2 mol/litre). For any single decomposition run, the plot of log (peroxide) against time showed a small curvature, and the apparent first order rate constants derived from this plot were dependent upon the concentration of peroxide, showing the presence of a reaction of higher order than first. Extrapolation of the rate constants obtained at different concentrations to zero concentration gave the true first order rate constant uncomplicated by secondary reactions. The extent of the higher order reaction decreased with increasing temperature and decreasing concentration.[6, 7] The extrapolated rate constants were used to obtain the activation energies and pre-exponential factors for peroxide decomposition both in the presence and in the absence of phenyl-α-naphthylamine. The activation energy and pre-exponential factor for peroxide decomposition in the absence of inhibitor at a peroxide concentration of 0·2 mol/litre were also obtained.

Oils containing various inhibitors at concentrations to give induction periods roughly twice those of the uninhibited oil at 160° C were also oxidized at different temperatures. The inhibitors used and their concentrations are given in Table I, together with the temperature range of the measurements and the apparent activation energy obtained from the induction period due to the inhibitor, *i.e.* from the difference in the induction period of the inhibited and uninhibited oil, $(t_{0\cdot5})_{INH} - (t_{0\cdot5})_{UNINH}$. It was observed that only the strongest inhibitors (α-naphthol and 2,2′-methylene-bis(4-methyl-6-*tert*-butyl phenol)) were completely consumed by $t_{0\cdot5}$, *i.e.* $(t_{1\cdot0} - t_{0\cdot5})$ for these inhibitors was equal at all temperatures to $(t_{1\cdot0} - t_{0\cdot5})$ for the uninhibited oil. None of the other inhibitors were completely consumed by $t_{1\cdot0}$, the values of $(t_{1\cdot0} - t_{0\cdot5})$, and therefore the relative amount of inhibitor unused increased in the order *N*-phenyl-β-naphthylamine, *N*-methylaniline, diphenylamine, aniline, cresol, phenol.

For *N*-methylaniline the measured values of $t_{0\cdot5}$ below 146° C increased more rapidly than would be expected from extrapolation of the high temperature results, which suggested that at the concentration used and below 146° C the amine was oxidized more rapidly than the oil and produced a more efficient inhibitor.[3] In order to check whether or not this occurs with any of the other inhibitors, measurements of the induction period were made on a steam bath at 100° C by a weighing technique.[8] Good agreement between the measured values of $t_{0\cdot5}$ and the values extrapolated from higher temperatures was obtained in all cases except for *N*-methylaniline and aniline, which were both much larger than predicted. It is therefore probable that below 134° C aniline, like *N*-methyl aniline, is oxidized to more powerful inhibitors more rapidly than it is consumed by reaction with peroxy radicals.

DISCUSSION

The usual reaction scheme for autoxidation is given below:

(I)	$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot}$		k_1
(II)	$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$		k_2
(III)	$RO_2^{\cdot} + RH \longrightarrow RO_2H + R^{\cdot}$		k_3
(IV)	$RO_2H \longrightarrow RO^{\cdot} + {}^{\cdot}OH$		k_4
(IV′)	$\left.\begin{matrix}RO^{\cdot}\\HO^{\cdot}\end{matrix}\right\} + RH \longrightarrow R^{\cdot} + \left\{\begin{matrix}ROH\\H_2O\end{matrix}\right.$		k'_4
(V)	$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow$ inactive products		k_5
(VI)	$RO_2^{\cdot} + IH \longrightarrow RO_2H + I^{\cdot}$		k_6
(VI′)	$\left.\begin{matrix}RO^{\cdot}\\HO^{\cdot}\end{matrix}\right\} + IH \longrightarrow I^{\cdot} + \left\{\begin{matrix}ROH\\H_2O\end{matrix}\right.$		k'_6
(VII)	$2RO_2^{\cdot} + IH \longrightarrow$ inactive products		k_7

RH represents the hydrocarbon, IH the inhibitor, and I$^{\cdot}$ the stable inhibitor radical. The *k*s represent the rate constants for the different reactions. The kinetic analysis on which this discussion is based is given in the appendix.

The Uninhibited Reaction

For the uninhibited oil it was assumed that the induction period was not due to the presence of minute traces of inhibitors present naturally in the oil. The assumption was probably justified, since the oil contained no unsaturated or aromatic compounds and no detectable sulphur, nitrogen, or oxygen compounds, nor was the induction period affected by percolation through active alumina. Moreover, an experiment was done in which a sample of oil was oxidized to the point at which autocatalysis began. It was then removed from the reaction cell, evacuated, and heated in a sealed tube for 24 hours at 180° C, after which virtually all the hydroperoxide would be decomposed. When the sample was reoxidized it had an induction period only 30 per cent less than the original oil.

The induction period of the uninhibited oil is given by Equation (4) in the appendix, and its temperature coefficient gives $\frac{1}{2}E_5 - E_3 - \frac{1}{2}E_1$. The measured activation energies obtained from the three definitions of the induction period are in good agreement, the mean value being 30·9 kcal/mol.

The temperature coefficient of the maximum rate of absorption of oxygen gives $2E_3 - E_5$ (Equation (8)). The assumption is generally made that E_5 is close to zero and can be neglected. This assumption is probably not quite true as a value for E_5 of 0·4 kcal/mol has been obtained for the recombination tetralyl peroxy radicals.[9] Moreover, it has been shown by Russell[10] that α-phenethylperoxy radicals interact to form non-radical products 1·9 times as readily as their α-deutero-derivatives, and it is, therefore, likely that this reaction also involves some activation energy. The activation energy of the propagation reaction (E_3) is therefore $\leqslant$ 10·2 kcal/mol. This value probably corresponds to the abstraction of a tertiary hydrogen atom from a saturated hydrocarbon, since the tertiary hydrogen atoms will be the most weakly bound hydrogen atoms in the oil. In this connexion it is interesting to note that the value obtained in this work is slightly less than the value obtained by Knorre *et al*[11] for abstraction of a secondary hydrogen from *n*-decane, and slightly greater than the values obtained for abstraction of hydrogen in the α position relative to an aromatic ring[9, 12, 13] or to a double bond.[12, 14]

Combining these two measured activation energies gives a value of 41·3 kcal/mol for E_1, the activation energy of the initiation reaction. We are not aware of any other values for the activation energy of this initiation reaction except for a rough value of 30 kcal/mol in a similar system,[15] which is obviously too low, and a value of 26 kcal/mol for the oxidation of ethyl linoleate.[16] The present value is in good agreement with the value predicted from bond dissociation energies. The hydrogen abstracted will most probably be a tertiary atom. The only value available for D(*tert* C–H) is 89 kcal/mol for *iso*butane.[17] D(H–O_2) has been determined to be 47 kcal/mol.[18] Assuming that D(*tert* C–H) for large molecules will also be about 89 kcal, ΔH for the reaction is therefore 42 kcal/mol, in excellent agreement with the measured activation energy.

It has frequently been pointed out[1] that the difficulty in obtaining information about Reaction (I) is that initiation from this reaction is only important at extremely low degrees of oxygen absorption. As soon as even a small concentration of hydroperoxide has been formed, further chain initiation will occur mainly by Reaction (IV). This problem has been overcome in the present case by working with an oil that contains little or no hydroperoxide. If the oil contained an appreciable amount of hydroperoxide there would be no induction period. Some initiation by Reaction (IV) is taken into account by the kinetic treatment, the only assumption being that during the induction period when no measurable amount of oxygen has been absorbed $k_4(RO_2H) \ll k_1$. In addition, k_1 in Equation (4) should really be written as $k_1(RH)(O_2)$ and the induction period should therefore be inversely proportional to the square root of the oxygen pressure, whereas if initiation was mainly due to peroxide there would be no dependence on oxygen pressure.[1] Experimentally, it was found that the induction period increased by factors of 1·3 and 2·0 when the oxygen pressure was reduced from one atmosphere to a half and to a fifth of an atmosphere respectively. These ratios are rather less than the predicted values of 1·4 and 2·2, the pressure dependence seeming to lie somewhere between one-half and one-third order. The pressure dependence was not a function of temperature. Its deviation from half order may be due to neglecting the hydroperoxide decomposition term in Equation (2), or to the occurrence of some cross termination at the lower oxygen pressures.

(VIII) $\quad R^{\cdot} + RO_2^{\cdot} \longrightarrow RO_2R$

Alternatively, at high oxygen pressures peroxy radicals may react with oxygen to give alkoxy radicals and ozone,[19] with a consequent reduction in the amount of hydroperoxide formed:

(IX) $\quad RO_2^{\cdot} + O_2 \longrightarrow RO + O_3$

Hydroperoxide Decomposition

The decomposition of alkyl hydroperoxides to give free radicals is a complex reaction owing to the presence of a secondary chain reaction.[7] In addition, the primary reaction can be second order under some conditions and first order under others.[1] Furthermore, it is frequently observed that the rate of decomposition of hydroperoxides is profoundly influenced by the nature of the solvent.[6] In the present work the peroxides produced in the oxidized oil were decomposed in the oxidate without separation in order that the solvent should be the same as when the peroxides were formed. In order to study the unimolecular decomposition of the hydroperoxides (*i.e.* Reaction (IV)), the rate of decomposition was studied as a function of concentration which permits the first order decomposition to be isolated from reactions of higher order. Previous workers[5, 6] have generally considered it necessary to add a chain terminating inhibitor to eliminate the chain decomposition. However, the rate constant at zero concentration of peroxide as obtained by extrapolation should be the rate constant of Reaction (IV) even in the absence of an inhibitor, since the chain reaction will be suppressed in sufficiently dilute solutions. The present results for peroxide decomposition show

this to be the case, the two rate constants being given by

$$k = 1{\cdot}3 \times 10^{12} \exp \frac{31{,}100}{RT} \text{ sec}^{-1}$$

and

$$k = 8{\cdot}3 \times 10^{11} \exp \frac{31{,}500}{RT} \text{ sec}^{-1}$$

for the uninhibited decomposition and for decomposition inhibited by 0·2 molar phenyl-α-naphthylamine, respectively. The average value of 31·3 kcal/mol for the activation energy of Reaction (IV) is in good agreement with earlier work for this reaction for a number of different hydroperoxides;[5, 6] it is also in agreement with the rough value of 33·7 kcal/mol obtained by Harle and Thomas [15] for the decomposition of the hydroperoxides of a similar white oil at two temperatures.

It should perhaps be pointed out that the activation energy we have determined for Reaction (IV) is very probably lower than the bond dissociation energy of the O–O bond, possibly because of solvent induced decomposition.[6] The true bond energy of an alkyl hydroperoxide would be expected to be between the value for hydrogen peroxide (48 kcal/mol [20]) and the recently recalculated values for dialkyl peroxides (34·0 to 37·5 kcal/mol).[21]

An alternative method of estimating $E_3 - \frac{1}{2}E_5$, based on the maximum rate of production of peroxide, has been worked out by Knorre *et al.*[11] The equation obtained differs from the equation for the maximum rate of absorption of oxygen in that hydroperoxide decomposition without the production of radicals must also be taken into account. Using the same nomenclature as is used in the appendix, the equations of Knorre *et al* become

(IV″) $\quad RO_2H \longrightarrow$ non-radical products $\quad k_4''$

$$(R(P))_{max} = \frac{k_3^2 k_4 (RH)^2}{2k_5 k_4''}$$

The activation energy for the maximum rate of production of peroxide $(R(P))_{max}$ was found to be about 32 kcal/mol. The determination of the activation energy of Reaction (IV″) is rather more difficult, since the measured activation energy of peroxide decomposition decreases with increasing peroxide concentrations, probably because of the increased importance of the chain reaction and the second order decomposition. The most reasonable value to use would seem to be the value obtained at a peroxide concentration equal to one-half of the maximum concentration of peroxide that is produced at a temperature in the middle of the range in which the decomposition was studied. This measured activation energy was 22·7 kcal/mol, the apparent first order rate constant being given by the $k = 10^8 \exp \frac{22{,}700}{RT}$ sec^{-1}. Substituting into the above expression and taking $E_4 = 31{\cdot}3$ kcal/mol, we find $E_3 - \frac{1}{2}E_5 = 11{\cdot}7$ kcal/mol, which, considering the difficulty in deciding just what value should be used for E_4'', is in reasonable agreement with the more accurate value obtained from oxygen absorption.

The Strongly Inhibited Reaction

The derivation of Equation (15) applies only to very strong inhibitors, since it is assumed that the induction period consists of two essentially independent parts, one lasting until the inhibitor is fully used up and consisting only of Reactions (I), (II), (IV), (IV′), (VI), and perhaps (VI′), and the other starting when the inhibitor is consumed and being the same as the induction period for the uninhibited oil. In other words, all peroxy radicals are removed by reaction with inhibitor and none react with hydrocarbon. Even if Reaction (III) is completely suppressed by the inhibitor, some hydroperoxide will have been formed by Reaction (VI), and therefore the second part of the induction period will be shorter than the uninhibited induction period. The magnitude of the error involved is hard to determine, but it is probably not large, since at the low inhibitor concentrations, where Equation (15) is valid, the two parts of the induction period are of equal orders of magnitude and the amount of hydroperoxide formed will be small.

At high concentrations of strong inhibitors Equation (15) no longer applies, the induction period now being proportional (Equation (16)) or roughly proportional (depending on whether Reaction (VI′) is included) to the square root of the inhibitor concentration. The error involved in the assumption of a two-part induction period is small, since the first part of the induction period is so much greater than the second part that the latter can be neglected without introducing a serious error (see Table I). The prediction that the induction period should be proportional to the square root of the concentration was rather surprising. It was confirmed for α-naphthol in the concentration range $5{\cdot}5 \times 10^{-5}$ to $6{\cdot}0 \times 10^{-4}$ g mol/litre and for phenyl-β-naphthylamine in the range $3{\cdot}6 \times 10^{-4}$ to $4{\cdot}0 \times 10^{-3}$ (Figs 1 and 2). It was not possible to go to higher concentrations to see if the order falls off still further as predicted by Equation (22), since the maximum concentrations used were saturated solutions at room temperature. A decrease in inhibitor efficiency with increasing inhibitor concentration has been reported previously;[22] it was attributed to a reaction between the inhibitor and oxygen, but it now appears that the decrease will occur even without such a reaction. It has also been reported [15] that inhibition by phenyl-β-naphthylamine causes a greater than linear increase of the induction period, with increasing inhibitor concentration. This might perhaps be due to oxidation of the inhibitor to more powerful

inhibitors, as seems to be the case with aniline and methylaniline.

Equations (15) and (16) should only be applied to strong inhibitors which are completely consumed by the end of the induction period. The only inhibitors studied in this work which fitted this requirement were α-naphthol and 2,2′-methylene-bis(4-methyl-6-*tert*-butyl phenol). An attempt to extend the results to other equally strong inhibitors failed because very few inhibitors are as efficient. Of those inhibitors which have been reported to be as good as α-naphthol, *i.e.*, hydroquinone, pyrogallol, trimethylhydroquinone, and 1,4 naphthohydroquinone,[23, 24] the first two were found to be virtually insoluble in oil; the latter two were not tested, since they react directly with oxygen even at 45° C.[23]

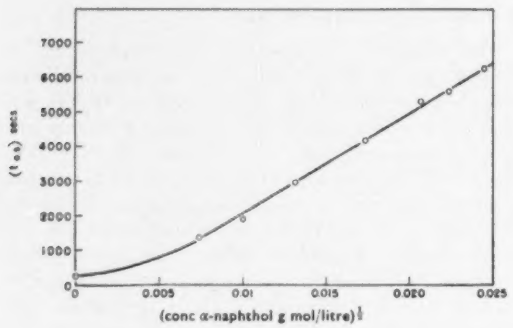

FIG 1

INDUCTION PERIOD OF α-NAPHTHOL INHIBITED OIL PLOTTED AGAINST THE SQUARE ROOT OF THE α-NAPHTHOL CONCENTRATION AT 182° C

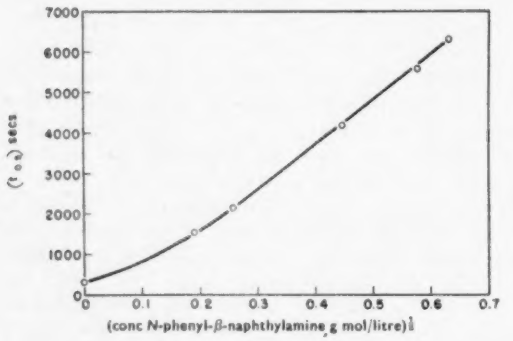

FIG 2

INDUCTION PERIOD OF PHENYL-β-NAPHTHYLAMINE INHIBITED OIL PLOTTED AGAINST THE SQUARE ROOT OF THE PHENYL-β-NAPHTHYLAMINE CONCENTRATION AT 179° C

The results obtained with α-naphthol (Table I) give two independent but consistent values for E_1, the activation energy of Reaction (I). At low concentrations $E = -E_1 = -41{\cdot}4$ kcal/mol. At high concentrations $E = -\frac{1}{2}E_1 - \frac{1}{2}E_4 = -36{\cdot}3$, or taking $E_4 = 31{\cdot}3$, $E_1 = 41{\cdot}3$ kcal/mol. These values agree with the value obtained from the uninhibited oxidation.

Although the inhibitor 2,2′-methylene-bis(4-methyl-6-*tert*-butyl phenol) is fully consumed by the end of the induction period, the region of changing kinetic order occurs over a very large range of concentration. The two concentrations at which the temperature coefficient of the induction period were measured were $5{\cdot}0 \times 10^{-5}$ and $3{\cdot}5 \times 10^{-3}$ g mol/litre and the kinetic orders were about 1·0 and 0·64 respectively. The use of higher concentrations than $3{\cdot}5 \times 10^{-3}$, where the kinetic order would presumably have been closer to 0·5, would have meant working at excessively high temperatures in order to get induction periods of reasonable length. The measured activation energy at the low concentration was 42·6 kcal/mol in fair agreement with the other values for E_1. At the high concentration a value of 37·9 kcal/mol was obtained, which in view of the high kinetic order is in reasonable agreement with the high concentration value for α-naphthol.

Equation (15) predicts that the induction period should be inversely proportional to the oxygen pressure, and Equation (16) predicts that it should be inversely proportional to the square root of the pressure. Unfortunately, experiment does not confirm these predictions, the ratios of the induction periods at high inhibitor concentration being 1·0 : 1·3 : 1·6 and at low concentrations 1·0 : 1·3 : 2·0 for oxygen pressures of one, one-half, and one-fifth of an atmosphere. Some complicating factor has, therefore, not been taken into account in the simplified treatment. A reaction between inhibitor and oxygen by which inhibitor is destroyed, *e.g.*

$$\text{(X)} \qquad IH + O_2 \longrightarrow I^{\cdot} + HO_2^{\cdot}$$

will not affect the predicted pressure relationships. It is instead necessary to have a reaction by which consumed inhibitor is regenerated, or a new inhibitor is formed, by reaction with oxygen or an oxygen-containing radical, *i.e.*

$$\text{(XI)} \qquad I^{\cdot} + \text{oxygen} \longrightarrow IH'$$

where IH′ may not be the same as the original inhibitor. Possible forms of Reaction (XI) might be

$$\text{(XII)} \qquad I^{\cdot} + HO_2^{\cdot} \longrightarrow IH + O_2$$

$$\text{(XIII)} \qquad I^{\cdot} + RO_2^{\cdot} \longrightarrow IH + O_2 + R'$$

Reaction (XI) will be in competition with other reactions which remove the inhibitor radical from the system; such as

$$\text{(XIV)} \qquad I^{\cdot} \longrightarrow \tfrac{1}{2}I_2$$

A kinetic treatment taking into account Reactions (XI) and (XIV) leads to the two equations

$$(15') \qquad t = \frac{(\mathrm{IH}^\circ)}{k_1(\mathrm{RH})(\mathrm{O_2})}\left(1 + \frac{k_{11}(\mathrm{O_2})}{k_{14}}\right)$$

$$(16') \qquad t = \frac{\sqrt{2}(\mathrm{IH}^\circ)^{\frac{1}{2}}}{k_1^{\frac{1}{2}}k_4^{\frac{1}{2}}(\mathrm{RH})^{\frac{1}{2}}(\mathrm{O_2})^{\frac{1}{2}}}\left(1 + \frac{k_{11}(\mathrm{O_2})}{k_{14}}\right)^{\frac{1}{2}}$$

These equations predict that the ratio of the induction periods for a given change in the oxygen pressure at high concentrations of inhibitor should be equal to the square root of the ratio at low concentrations. This result is closer to the experimental observation, but it is still not completely correct. A better agreement with experiment would probably be obtained if Reaction (XIV) were written as the bimolecular reaction which it undoubtedly is.

$$(\mathrm{XV}) \qquad 2\mathrm{I}^\cdot \longrightarrow \mathrm{I_2}$$

but in this case the kinetics are too complicated to solve in a useful form. The dependence of the induction period on oxygen pressure did not vary appreciably with temperature, and therefore the measured activation energies do not need correcting for the temperature coefficient of the term $\frac{k_{11}}{k_{14}}(\mathrm{O_2})$. The activation energies E_{11} and E_{14} must be small and roughly equal. Moreover, the temperature coefficient of solubility of oxygen in the oil must also be small, as has been reported previously.[25]

The activation energies with an inhibitor of intermediate activity which is not completely consumed by the end of the induction period, *N*-phenyl-β-naphthylamine, were intermediate between the results for the strongly inhibited oils and for the uninhibited oil.

The Weakly Inhibited Reaction

The kinetic treatment for very weak inhibitors given in the appendix follows the mechanism suggested by Boozer and Hammond.[26, 27] The same assumption that the induction period can be divided into two independent parts is made, but in this case the assumption is much more drastic, since the inhibitor is not all consumed by the end of the induction period. A complete kinetic analysis involving termination by both Reactions (V) and (VII) is, however, too complicated to be of much use. In addition to this difficulty, there is an experimental difficulty in that, with the exception of diphenylamine, the weak inhibitors studied have rather low boiling points and are, therefore, quite volatile in the temperature ranges under study. Furthermore, aniline and *N*-methyl aniline are both oxidized to more powerful inhibitors so that the activation energy plot is really a curve, not a straight line, and the values given in Table I for these compounds are unquestionably too high.

In view of the kinetic results at high concentrations of strong inhibitors, a question remains as to the validity of the Boozer and Hammond mechanism for weak inhibitors. Some light is shed on this problem by examining the activation energies of the induction periods of the oils inhibited with phenol, *o*-cresol, and diphenylamine. The values are roughly 31 kcal/mol or less, which suggests that in spite of the assumptions involved in its derivation, the induction period is more closely represented by Equation (30) than by Equation (16), since in the latter case an activation energy between 31 and 36 kcal/mol would be expected. Probably, therefore, weak inhibitors terminate chains by Reaction (VII) and not by Reaction (VI). Absolute values of the activation energies of the termination reaction cannot safely be derived, except perhaps in the case of the non-volatile inhibitor diphenylamine, where a value

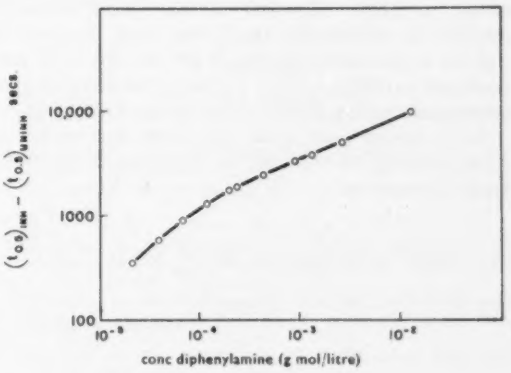

FIG 3

INDUCTION PERIOD DUE TO DIPHENYLAMINE $(t_{0.5})_{INH} - (t_{0.5})_{UNINH}$ PLOTTED AGAINST THE DIPHENYLAMINE CONCENTRATION

of $E_7 - E_5 = 1{\cdot}2$ kcal/mol was found. However, it is interesting to note that deuterated phenol and *o*-cresol have lower measured activation energies and therefore higher values for E_7 than the respective unsubstituted compounds. These differences are in the right direction but are larger in magnitude than would be expected.[28]

Some further information on the question of mechanism was obtained by examining the induction period of the oil inhibited with diphenylamine at very low inhibitor concentrations. This inhibitor was chosen for study as it was the strongest inhibitor examined that showed roughly half order dependence of the induction period on inhibitor concentration in the range previously studied.[3] It was, therefore, possible to extend the range of study into the concentration region where strong inhibitors show first order dependence. The induction period due to the inhibitor is shown plotted against the concentration in Fig 3; it can be seen that at a concentration below

$1{\cdot}5 \times 10^{-4}$ g mol/litre the order of the inhibition process starts to increase. A re-examination of the Boozer and Hammond mechanism[26,27] gives an explanation for this phenomenon.

The inhibition mechanism proposed by Boozer and Hammond involves the reactions

$$RO_2^{\cdot} + IH \underset{b}{\overset{a}{\rightleftarrows}} (RO_2^{\cdot}IH)$$

$$RO_2^{\cdot} + (RO_2^{\cdot}IH) \xrightarrow{c} \text{inactive products}$$

A simple kinetic treatment of these equations yields the relation

$$(RO_2^{\cdot}) \propto (IH)^{-1}$$

i.e. the induction period (which is proportional to the reciprocal of the rate of propagation) is proportional to $(IH)^{1}$. However, if the concentration of inhibitor is sufficiently small, the back reaction (*b*) will be suppressed and $(RO_2^{\cdot})$ will be inversely proportional to (IH), *i.e.* there will be a first order relation between induction period and inhibitor concentration.

Both strong and weak inhibitors can therefore quite probably be regarded as inhibiting by the same basic mechanism.

$$RO_2^{\cdot} + IH \underset{b}{\overset{a}{\rightleftarrows}} (RO_2^{\cdot}IH) \xrightarrow{d} RO_2H + I^{\cdot}$$
$$\Big| RO_2^{\cdot}$$
$$\xrightarrow[c]{} \text{inactive products}$$

Very strong inhibitors, such as α-naphthol, which are completely consumed by the end of the induction period, give high activation energies, and probably reduce the chain length to one, act by the pathway *ad*. The rate constant of the back reaction k_b must be much less than k_d. Inhibitors of intermediate activity, such as phenyl-β-naphthylamine, which are not completely consumed during the induction period and which give low activation energies may react by either *abd* or *abc* with, in the first case, $k_d < k_b$ and, in the second case, the rate of reaction *c* being greater than *b* at low concentrations of inhibitor and less than *b* at high concentrations. Although the kinetics of inhibition by weak inhibitors can be explained by either pathway, the observation that weak inhibitors show a deuterium isotope effect[3] proves that reaction *c* is of greater importance than reaction *d*. The absence of an isotope effect with strong inhibitors is readily understandable. With inhibitors of intermediate activity, the absence of an isotope effect means either that reaction occurs by *abd* or that the activation energy of reaction *c* is very low. The relative efficiencies of inhibitors will depend on the relative rates of the four reactions, and in the case of very strong inhibitors the complex $(RO_2^{\cdot}IH)$ might merely represent the activated complex and not a stable intermediate.

ACKNOWLEDGMENTS

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APPENDIX

Kinetics of the Uninhibited Oil Oxidation

For the uninhibited oxidation the same derivation as that proposed by Harle and Thomas is used.[15] From the reaction scheme given previously:

$$(1) \qquad \frac{d(RO_2^{\cdot})}{dt} = k_1 + k_4(RO_2H) - k_5(RO_2^{\cdot})^2 = 0$$

$$(2) \qquad \frac{d(RO_2H)}{dt} = k_3(RO_2^{\cdot})(RH) - k_4(RO_2H)$$
$$= \frac{k_3(RH)}{k_5^{\frac{1}{2}}}(k_1 + k_4(RO_2H))^{\frac{1}{2}} - k_4(RO_2H)$$

At the start of the reaction $k_4(RO_2H)$ is small and can be neglected in comparison with the first term. Integration gives

$$(3) \qquad t = \frac{2k_1^{\frac{1}{2}}k_5^{\frac{1}{2}}}{k_3k_4(RH)}\left[\left(1 + \frac{k_4(RO_2H)}{k_1}\right)^{\frac{1}{2}} - 1\right]$$

and if $\dfrac{k_4(RO_2H)}{k_1} \ll 1$

$$(4) \qquad t = \frac{k_5^{\frac{1}{2}}(RO_2H)}{k_1^{\frac{1}{2}}k_3(RH)}$$

This equation gives the induction period of the uninhibited oil defined as the time required for a certain small concentration of RO_2H to be formed, or alternatively, since RO_2H is the initial stable product of oxidation, the induction period can also be defined as time required for the oil to absorb a small but definite amount of oxygen. The temperature coefficient of the induction period is, therefore, given by $\frac{1}{2}E_5 - E_3 - \frac{1}{2}E_1$.

The rate of absorption of oxygen (R_{O_2}) is given by

$$(5) \qquad (R_{O_2}) = k_1 + k_2(O_2)(R^{\cdot})$$

$$(6) \qquad (R_{O_2}) = 2k_1 + 2k_4(RO_2H) + k_3(RH)(RO_2^{\cdot})$$

assuming the products from Reaction (IV) both start oxidation chains. When a steady state concentration of (RO_2H) is established $\dfrac{d(RO_2H)}{dt} = 0$ and the rate of absorption of oxygen is a maximum.

From Equation (2)

$$(7) \qquad (RO_2H) = \frac{k_3^2(RH)^2}{2k_4k_5}\left[1 + \left(1 + \frac{4k_1k_5}{k_3^2(RH)^2}\right)^{\frac{1}{2}}\right]$$

Substituting into Equation (6), since $4k_1k_5 \ll k_3^2(RH)^2$

$$(8) \qquad (R_{O_2})_{max} \approx \frac{3k_3^2(RH)^2}{k_5}$$

and therefore the temperature coefficient of $(R_{O_2})_{max}$ gives approximately $2E_3 - E_5$.

Kinetics of Strongly Inhibited Oil Oxidation

Chain termination is assumed to occur solely by Reaction (VI) as long as the inhibitor lasts. In other words, it is assumed that the total induction period consists of two essentially independent parts, one (t_{INH}) lasting until the inhibitor is fully used up and the other starting when all the inhibitor is consumed and being the same as the induction period for

the uninhibited oil (t_{UNINH}). Applying the steady state method during t_{INH}:

$$(9) \qquad (RO_2^{\cdot}) = \frac{k_1 + k_4(RO_2H)}{k_5(IH)}$$

$$(10) \qquad \frac{d(RO_2H)}{dt} = k_5(RO_2^{\cdot})(IH) - k_4(RO_2H) = k_1$$

$$(11) \qquad \therefore (RO_2H) = k_1 t$$

$$(12) \qquad \frac{-d(IH)}{dt} = k_5(RO_2^{\cdot})(IH) = k_1 k_4 t + k_1$$

$$(13) \qquad \therefore -(IH) = \tfrac{1}{2}k_1 k_4 t^2 + k_1 t - (IH^{\circ})$$

where (IH°) = the initial concentration of inhibitor. At the end of the inhibited induction period $(IH) = 0$

$$(14) \qquad \therefore t_{INH} = -\frac{1}{k_4}\left[1 \pm \left(1 + \frac{2k_4(IH^{\circ})}{k_1}\right)^{\frac{1}{2}}\right]$$

In order that t_{INH} should be proportional to the first power of the initial inhibitor concentration, $2k_4(IH^{\circ})$ must be much less than k_1.

$$(15) \qquad \therefore t_{INH} \simeq \frac{(IH^{\circ})}{k_1}$$

The temperature coefficient of t_{INH} therefore gives approximately $-E_1$. If $2k_4(IH^{\circ}) \gg k_1$ half order kinetics are obtained; and the induction period is given by

$$(16) \qquad t_{INH} \simeq \frac{\sqrt{2}(IH^{\circ})^{\frac{1}{2}}}{k_1^{\frac{1}{2}}k_4^{\frac{1}{2}}}$$

and the measured temperature coefficient will give $-\frac{1}{2}E_1 - \frac{1}{2}E_4$.

In the derivation of Equation (15) it was assumed that Reaction (IV′) was fast. However, a reaction analogous to Reaction (VI), *i.e.* Reaction (VI′) may remove all the alkoxy and hydroxy radicals before they reacted with RH. In this case

$$(17) \qquad (RO_2^{\cdot}) = \frac{k_1}{k_5(IH)}$$

$$(18) \qquad (RO^{\cdot}) = \frac{k_4(RO_2H)}{k'_5(IH)}$$

$$(19) \qquad \frac{d(RO_2H)}{dt} = k_1 - k_4(RO_2H)$$

$$(20) \qquad \therefore (RO_2H) = \frac{k_1}{k_4}(1 - e^{-k_4 t})$$

$$(21) \qquad \frac{-d(IH)}{dt} = k_5(RO_2^{\cdot})(IH) + k'_5(RO^{\cdot})(IH) = k_1(2 - e^{-k_4 t})$$

Integrating, and putting $(IH) = 0$ at the end of the induction period

$$(22) \qquad 2t_{INH} + \frac{1}{k_4}(e^{-k_4 t_{INH}} - 1) = \frac{(IH^{\circ})}{k_1}$$

Expanding the exponential and neglecting all terms except the first and second, one again finds $t_{INH} \simeq \frac{(IH^{\circ})}{k_1}$. Or, taking into account the first three terms of the exponential, Equation (16) is again obtained.

Kinetics of Weakly Inhibited Oil Oxidation

It is again assumed that the induction period can be divided into two independent parts, chain termination in the first part (t_{INH}) being due solely to Reaction (VII). Applying the steady state method during t_{INH}

$$(23) \qquad (RO_2^{\cdot}) = \frac{(k_1 + k_4(RO_2H))^{\frac{1}{2}}}{k_7^{\frac{1}{2}}(IH)^{\frac{1}{2}}}$$

$$(24) \qquad \frac{d(RO_2H)}{dt} = \frac{k_3(RH)}{k_7^{\frac{1}{2}}(IH)^{\frac{1}{2}}}(k_1 + k_4(RO_2H))^{\frac{1}{2}} - k_4(RO_2H)$$

$$(25) \qquad \therefore \frac{d(RO_2H)}{dt} \simeq \frac{k_3(RH)}{k_7^{\frac{1}{2}}(IH)^{\frac{1}{2}}}(k_1 + k_4(RO_2H))^{\frac{1}{2}}$$

$$(26) \qquad \frac{-d(IH)}{dt} = k_7(IH)(RO_2^{\cdot})^2 = k_1 + k_4(RO_2H)$$

$$(27) \qquad \therefore \frac{-d(RO_2H)}{d(IH)} \simeq \frac{k_3(RH)}{k_7^{\frac{1}{2}}(IH)^{\frac{1}{2}}} \cdot \frac{1}{(k_1 + k_4(RO_2H))^{\frac{1}{2}}}$$

(28) Hence

$$(IH)^{\frac{1}{2}} \simeq (IH^{\circ})^{\frac{1}{2}} - \frac{k_7^{\frac{1}{2}}}{3k_3k_4(RH)}(k_1 + k_4(RO_2H))^{\frac{3}{2}} + \frac{k_7^{\frac{1}{2}}k_1^{\frac{1}{2}}}{3k_3k_4(RH)}$$

Substituting into Equation (25) and integrating,

$$(29) \qquad \frac{k_3(RH)t}{k_7^{\frac{1}{2}}} \simeq \left(\frac{2k_1^{\frac{1}{2}}(IH^{\circ})^{\frac{1}{2}}}{k_4} + \frac{2k_7^{\frac{1}{2}}k_1^{\frac{3}{2}}}{3k_4^2k_3(RH)}\right)\left[\left(1 + \frac{k_4(RO_2H)}{k_1}\right)^{\frac{1}{2}} - 1\right] - \frac{k_7^{\frac{1}{2}}k_1^{\frac{3}{2}}}{6k_4^2k_3(RH)}\left[\left(1 + \frac{k_4(RO_2H)}{k_1}\right)^{2} - 1\right]$$

For small values of $\frac{k_4}{k_1}(RO_2H)$, *i.e.* during the induction period (t_{INH}) when (RO_2H) is small, Equation (29) reduces to:

$$(30) \qquad t_{INH} \simeq \frac{k_7^{\frac{1}{2}}}{k_1^{\frac{1}{2}}k_3} \cdot \frac{(IH^{\circ})^{\frac{1}{2}}}{(RH)} \cdot (RO_2H)$$

Assuming that the concentration of RO_2H at t_{INH} is the same at all temperatures, the temperature coefficient of t_{INH} is approximately $\frac{1}{2}E_7 - \frac{1}{2}E_4 - E_3$.

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PROCESSING OF LOW TEMPERATURE TAR OIL FRACTIONS TO DIESEL OILS *

By S. K. BOSE,† A. K. GANGULI,† N. G. BASAK,† and A. LAHIRI † (Fellow)

INTRODUCTION

SINCE world war II there has been a continuous increase in the demand for middle distillates of petroleum fuels in all countries. The demand for these fuels is, however, disproportionately high for the undeveloped countries which are now being rapidly industrialized. In India the imbalance between production and demand of diesel oils has reached serious proportions, leading to heavy imports of kerosine and diesel oils, and it is expected that by 1960 there will be a deficit of over 2·5 million tons of middle distillates per annum. This imbalance will further worsen as the Indian Railways progressively adopt dieselization for a substantial portion of their traffic in order to cope with the increasing loads and particularly in view of limited supplies of good quality coal.

On the other hand, production of domestic coke by low temperature carbonization of coal is likely to be widely undertaken in future in order to meet a part of the 100 million-ton coal equivalent of the domestic demand, which is at present being chiefly met by wood, animal dung, and farm wastes.[1] Further, developments in the U.S.A. and elsewhere indicate that fluidized carbonization may become a commercial proposition, when it can be expected that a large portion of coal, now being burnt raw in the powdered form in thermal power plants or synthesis gas plants, will be replaced by char. Both these steps will release large quantities (about 8–10 per cent of coal carbonized) of low temperature tar of a primary character. These tars are very different from the normal high temperature coke oven tars and call for new technology to process them.

Since a ton of diesel oil is equivalent to 8 to 10 tons of coal, due to the higher efficiency in use of the former, say in a locomotive, the processing of coal by low temperature carbonization, either in fixed or fluid bed, will substantially increase the ultimate efficiency in the use of coal, providing a reactive solid fuel for domestic, power, or industrial purposes, on the one hand, and a package fuel by processing of the tar, on the other, for traction, agriculture, and mining. A programme of research has therefore been undertaken at the Central Fuel Research Institute of India to investigate possibilities for utilization of low temperature carbonization tars from coals, in particular for processing to suitable grades of diesel fuels.

PREVIOUS WORK

Conversion of low temperature tar into suitable grades of diesel oil is not easy in view of the refractory and aromatic nature of the feed material.

In Germany, during the second world war, two processes were developed (TTH and MTH processes) for converting brown coal tars into diesel oil. It was claimed that tar oils could be hydrogenated in a single stage in the liquid phase over fixed-bed catalysts using a plant practically identical to that used for vapour-phase hydrogenation. For these processes the feed oil should not contain any material that might poison the catalyst, and polymerization of intermediate unsaturated products should be restricted in order to avoid formation of catalyst-poisoning substances.

The catalysts used for these processes were pelleted WS_2 and mixtures of WS_2, NiS, and Al_2O_3. The operating pressure was 300 atm and average reaction temperature was 360° C in the TTH process and 390° C in the MTH process. Tar feed rate was 1 metric ton/hr/m³ catalyst in the TTH process and about 0·6 metric ton/hr/m³ catalyst in the MTH process.[2]

About 95 per cent of the feed and 90–92 per cent crude product were obtained respectively from the TTH and the MTH processes. The products obtained are as follows:

	TTH (%)	MTH (%)
Petrol	25	35
Diesel oil	50	60
Refined wax	10–15	—
Lubricating oil	10–15	—

Recently, BASF, West Germany, has developed [3] a two-stage process. Low temperature brown coal tar is processed in the liquid phase at 250 atm partial pressure of H_2 and at 460°–470° C with addition of about 0·5 per cent of a catalyst consisting of an activated lignite semi-coke with molybdenum. The liquid phase product distilled up to 350° C, called middle oil (yield 42 per cent by weight), is further hydrogenated in the vapour phase over pelleted catalysts at 240 partial pressure of H_2 at 408° C. The yield of diesel oil amounts to 55 per cent with an aniline point of 64° C and Cetane No. of 47.

According to another patented process, known as

* MS received 21 January 1959.

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the Varga process,[4] German brown coal tar is treated in the liquid and vapour phase in single stage (*i.e.* without intermediate cooling, condensation, and distillation) at a partial pressure of H_2 of 70 atm. 77 per cent yield of diesel oil has been claimed by this process. The product is, however, of inferior grade, the aniline point being 46·6° C and Diesel Index No. 32.

The Central Fuel Research Institute of India has been carrying out investigations for evolving suitable catalysts for the production of light and high-speed diesel oil from low temperature tar at low pressure ranging from 50 to 200 atm, and some results of these investigations are reported in this paper.

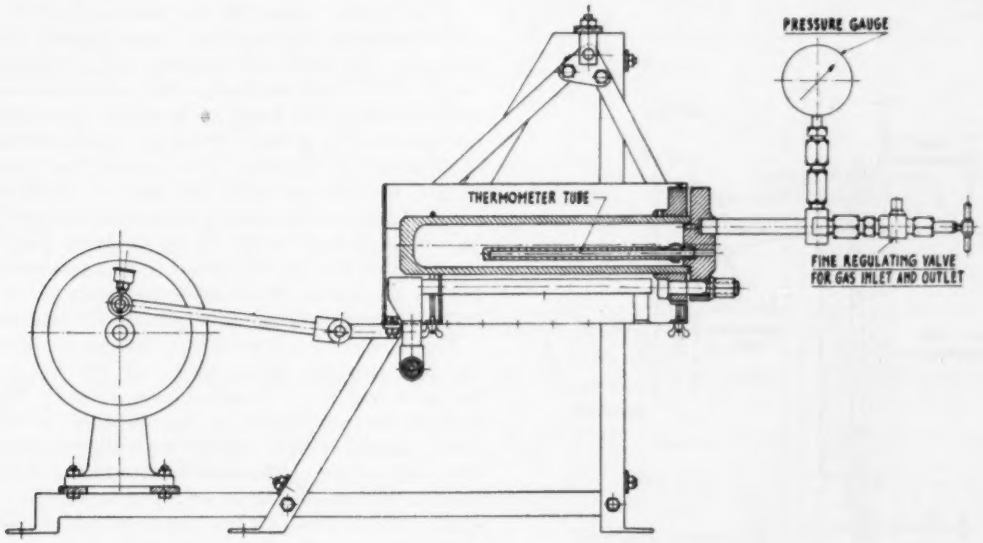

FIG 1
HIGH PRESSURE AUTOCLAVE

EQUIPMENT, RAW MATERIALS, AND METHOD

Investigations have been carried out both in high pressure autoclaves and continuous bench scale reactors. The equipment used is described below.

Equipment

A sketch of the high pressure autoclave is given in Fig 1. Fig 2 shows the continuous bench scale apparatus. The capacity of the reactor is 150 cc. The operation is carried out in a single stage, and no recycling of H_2 or oil (product) is done.

Catalyst

The catalysts * used are complex mixtures containing two or more of the following metals: nickel, cobalt, aluminium, molybdenum, and chromium as oxides or sulphides with or without carrier. The performance of some of the catalysts is recorded here.

Raw Material

Low temperature carbonization tar obtained from a low temperature carbonization plant of a high moisture Raniganj coal (82 per cent C) was used for these experiments. The physical and chemical properties of this tar are tabulated in Tables I and II.

TABLE I
Distillation Characteristics and Tar Acids and Bases Content of the Upper Kajora Tar

Fractions	Yield, %	Tar acids, % of the fractions	Bases, % of the fraction	Neutral, % of the fraction
Up to 200° C .	8·96	30·0	2·0	68·0
200°–250° C .	41·52	43·5	3·0	53·5
250°–300° C .	25·64	40·0	9·0	51·6
300°–350° C .	14·38	30·0	7·4	62·6
Residue and loss	9·50	—	—	—

The tar was distilled into the following fractions: (*a*) up to 200° C; (*b*) 200°–250° C; (*c*) 250°–300° C; (*d*) 300°–350° C.

The individual fractions were hydrogenated under various conditions of reaction.

* The catalysts used in this investigation are the subject of pending patent applications.

TABLE II

Physical and Chemical Properties of the Tar Oil Fractions

Properties	200°–250° C	250°–300° C	300°–350° C
Sp gr at 60° F	0·876	0·934	0·968
Viscosity at 100° F (Redwood No. 1), sec	30·26	36·6	47·8
Flash point (Pensky–Martens closed), °F	150·0	174·0	142·0
Aniline point, ° C	25·6	26·8	37·2
Conradson carbon residue, %	0·047	0·092	0·125
Saturates, %	11·0	12·0	24·0
Unsaturates, %	17·5	3·0	23·0
Aromatics, %	71·5	84·0	52·0
Sulphur, %	0·34	—	—

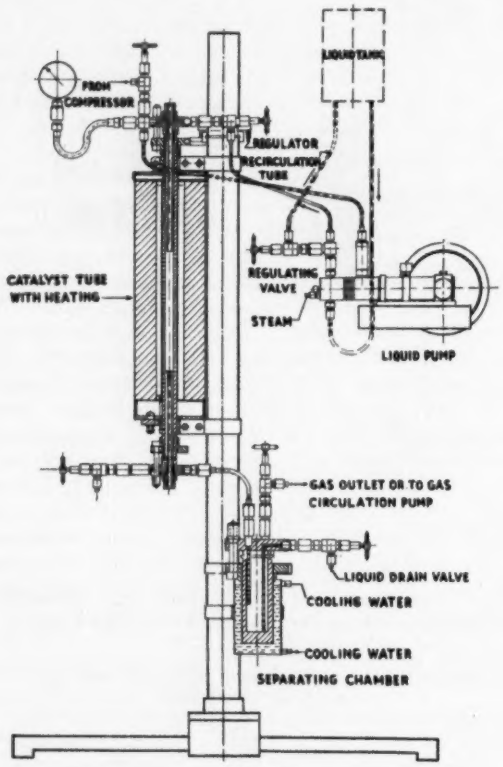

FIG 2

CONTINUOUS BENCH SCALE APPARATUS

(1) *Hydrogenation of Selected Fractions (Untreated); (a) 250°–300° C; (b) 300°–350° C of Low Temperature Tar Oil with* Ni–Al *Catalyst in Batch Autoclaves*

In these experiments tar oil fractions containing tar acids and bases were subjected to hydrogenation. The products of hydrogenation were distilled in two fractions: (i) fraction boiling up to 200° C; (ii) fraction 200°–350° C. The fraction 200°–350° C was designated as "diesel oil." On evaluation of products from different runs it was observed that the physical properties, *i.e.* specific gravity, viscosity, flash point, Conradson coke residue, remained more or less constant and satisfied the specifications of standard diesel oil. Only the aniline point varied from product to product, due to the varying content of aromatics in the products. In the routine testing of the products from the autoclave tests, therefore, only aniline point, aromatics, and saturated and unsaturated hydrocarbons were determined for comparing the products of different experiments.

These results (Table III) indicate that the 250°–300° C fraction of tar oil can be satisfactorily processed to good quality diesel oil (as characterized by the aniline point) at high catalyst concentration (10 per cent) and high initial cold pressure of hydrogenation, and at 400° C temperature. The conversion of tar acids and bases was found to be almost quantitative, and the resulting product contained a high percentage of saturates (72 per cent), thus contributing towards raising the aniline point of 56·6° C. With progressively decreasing catalyst concentrations and at a higher temperature of 450° C, the yield and quality of the diesel oil fraction was found to be unsatisfactory, but the conversion of tar acids and bases to hydrocarbons were still found to be complete in all cases.

The conversion of 300°–350° C fraction to diesel oil was not, however, satisfactory. At 450° C some of the acids and bases remained unconverted. Higher temperature contributed to high yield of oil boiling within gasoline range, with corresponding decrease in diesel oil fraction. The aniline point of the diesel oil fraction was also found to be lower at 450° C. The quality of the diesel oil fraction from 300° to 350° C tar fraction was, however, inferior in all cases.

(2) *Studies on the Hydrogenation of Neutral Oil Fractions* (a) 200°–250° *C*, (b) 250°–300° *C*, (c) 300°–350° *C of a Low Temperature Tar Oil in Batch Autoclave*

The following studies were made with neutral tar oil fractions with a view to evaluating the activity of: (i) Ni–Al reduced catalyst; (ii) Ni–Al oxide catalyst in conjunction with CS_2 added to oil; and (iii) Ni oxide precipitated on kieselguhr with and without addition of carbon disulphide to the feed oil.

Tar acids and bases were separated by repeated alternate extraction with 20 per cent NaOH and 10 per cent H_2SO_4 saturated with sodium chloride. The results are tabulated in Table IV. With the decreasing amount of catalyst the quality of the diesel oil fraction produced was poor with respect to aniline point. Yield of diesel oil fraction from 200°–250° C feed amounted to 53·5 per cent with catalyst (i); the yield increases progressively from 69·3 per cent with catalysts (ii) and (iii) under identical conditions of reaction. The aniline point of the products ranged from 38° to 40° C only.

For tar fractions 250°–300° C, slightly higher yields

TABLE III

Operating Variables and Characteristics of Products of Hydrogenation of Untreated Tar Oil Fractions (a) 250°–300° *C*, (b) 300°–350° *C from Upper Kajora Low Temperature Tar*

Samples hydrogenated	Upper Kajora low temperature tar fraction (250°–300° C) untreated (containing tar acids and bases)						Upper Kajora low temperature tar fraction (300°–350° C) untreated (containing tar acids and bases)			
Experiment No.	Analysis of feed-stock sample	H(c)-150	H(c)-151	H(c)-153	H(c)-154	H(c)-155	Analysis of feed-stock sample	H(c)-156	H(c)-157	H(c)-158
Catalyst	—	$Ni–Al_2O_3$ (10%)	$Ni–Al_2O_3$ (4·3%)	$Ni–Al_2O_3$ (6·5%)	$Ni–Al_2O_3$ (7·5%)	$Ni–Al_2O_3$ (5·6%)	—	$Ni–Al_2O_3$ (5·5%)	$Ni–Al_2O_3$ (4·8%)	$Ni–Al_2O_3$ (4·9%)
Temperature, ° C	—	400	400	400	400	450	—	400	400	450
Reaction time, hr	—	5	5	4	4	4	—	4	4	4
Initial hydrogen pressure, kg/cm²	—	130	128	100	100	100	—	100	100	100
Reaction pressure, kg/cm²	—	253	278	213	222	228	—	215	220	233
Yield of product, %	—	88·4	94·1	90·4	87·6	81·3	—	92·0	92·5	84·6
Tar acids in product, %	40	Traces	2·0	2·6	1·3	0·4	30·0	12·5	15·2	Traces
Tar bases in product, %	9·4	Traces	1·0	1·4	0·6	0·3	7·4	4·6	4·4	2·5
Neutral oil, in product %	51·6	99·0	97·0	92·1	97·6	95·0	62·6	82·6	79·7	95·8
Loss in extraction, %	—	1·0	—	3·9	0·5	4·3	—	0·6	0·7	1·7
Product boiling up to 200° C, %	—	30·0	25·5	26·25	24·4	51·3	—	8·1	—	36·0
Product boiling 200°–350° C, % on neutral oil	—	57·0	62·0	72·50	72·5	40·5	—	73·0	—	48·0
Properties of neutral oil boiling between 200°–350° C:										
Aniline point, ° C	26·8	56·6	38·4	45·8	47·8	18·0	37·2	43·8	41·2	21·0
Saturates, %	3·0	72·0	58·0	54·0	54·0	—	23·0	38·0	—	32·0
Unsaturates, %	12·0	2·0	4·0	6·0	4·0	—	24·0	4·0	—	4·0
Aromatics, %	84·0	26·0	38·0	40·0	42·0	—	52·0	58·0	—	64·0
Sp gr, 60°/60° F	—	0·845	0·846	0·860	0·875	0·875	—	—	—	0·875
Diesel index	—	47·0	35·8	38·4	35·5	19·4	—	—	—	21·0

TABLE IV

Operating Variables and Characteristics of Products of Hydrogenation of Neutral Tar Oil (a) 200°–250° *C*, (b) 250°–300° *C*, (c) 300°–350° *C from Upper Kajora Low Temperature Tar—Effect of Different Catalysts*

Samples hydrogenated	Upper Kajora neutral tar oil fraction (200°–250° C)					Upper Kajora neutral tar oil fraction (250°–300° C)			Upper Kajora neutral tar oil fraction (300°–350° C)		
Experiment No.	Analysis of feed-stock	H(c)-160	H(c)-163	H(c)-166	H(c)-167	Analysis of feed-stock	H(c)-161	H(c)-164	Analysis of feed-stock	H(c)-162	H(c)-165
Catalyst	—	Reduced $Ni–Al_2O_3$ (3·2%)	$Ni–Al_2O_3$ with CS_2 (3·0%)	Ni–Kieselguhr with CS_2 in oil (2·0%)	Ni–Kieselguhr (2·0%)	—	Reduced $Ni–Al_2O_3$ (3·4%)	$Ni–Al_2O_3$ with CS_2 in oil (3·0%)	—	Reduced $Ni–Al_2O_3$ (3·03%)	$Ni–Al_2O_3$ with CS_2 (3·0%)
Temperature, ° C		400	400	400	400	—	400	400	—	400	400
Pressure, kg/cm² (cold)	—	100	100	100	100	—	100	100	—	100	100
Reaction pressure, kg/cm²	—	223	225	227	228	—	227	223	—	220	220
Reaction time, hr	—	3	3	3	3	—	3	3	—	3	3
Product obtained, %	—	93·5	92·5	92·6	90·5	—	91·8	93·7	—	92·2	94·7
Fraction up to 200° C, % on product	—	23·3	30·02	14·9	21·7	—	10·28	4·09	—	5·4	4·5
Fraction (200°–350° C), % on product	—	53·5	65·5	79·3	70·9	—	85·69	91·06	—	70·3	69·67
Residue and loss, %	—	22·9	4·48	5·7	7·4	—	3·03	3·85	—	24·3	25·8
Properties of oil boiling between 200°–350° C:											
Aniline point, ° C	25·6	38·8	40·6	39·0	33·8	26·8	38·8	42·6	37·2	37·4	40·6
Saturates, %	11·0	54·0	52·0	44·0	52·0	3·0	38·0	42·0	23·0	32·0	—
Unsaturates, %	17·5	2·0	4·0	6·0	6·0	12·0	6·0	6·0	24·0	8·0	—
Aromatics, %	71·5	44·0	44·0	50·0	42·0	84·0	56·0	52·0	52·0	60·0	—
Sp gr (60° F)	0·876	0·865	0·860	0·870	0·865	0·934	0·890	0·885	0·968	0·930	—
Diesel index	23·4	32·5	34·9	32·0	29·7	15·9	28·0	30·5	14·6	20·4	—

of diesel oil fraction were observed when using catalyst (ii). The aniline point of the sample ranged from 38·8° to 42·6° C. Similar results were obtained with 300°–350° C tar fractions.

(3) *Studies on the Hydrogenation of Neutral Oil Fractions* (a) 200°–250° *C*, (b) 250°–300° *C*, (c) 300°–350° *C of Tar Oil Using Catalyst of Sulphide of a Metal of the Sixth Group in Batch Autoclave —Catalyst* 112

Investigation on the evaluation of different catalysts was continued, and catalyst 112 was used in this series of experiments. The results are tabulated in Table V. At 4 per cent catalyst concentration the yield of diesel oil from the 250°–300° C fraction of neutral oil contained 73 per cent saturates with an aniline point of 54·6° C. With decreasing amount of catalyst slightly inferior products resulted. Yield of diesel oil from the 200°–250° C oil fraction generally amounted to 45 per cent, with corresponding increase in aniline point from 45·4° to 54° C when catalyst concentration was increased from 2 to 4 per cent.

Although the products from experiments H-136 and H-137 contained identical quantities of aromatics

TABLE V

Operating Variables and Characteristics of Products of Hydrogenation of Neutral Tar Oil (a) 200°–250° *C*, (b) 250°–300° *C*, (c) 300°–350° *C from Upper Kajora Tar—Effect of Catalyst Concentration using Catalyst* 112

Samples hydrogenated	Upper Kajora neutral tar oil (200°–250° C)			Upper Kajora neutral tar oil (250°–300° C)			Upper Kajora neutral tar oil (300°–350° C)		
Experiment No.	Feed-stock analysis	H-136	H-137	Feed-stock analysis	H-138	H-139	Feed-stock analysis	H-140	Ha-141
Catalyst	—	Cat 112 (2%)	Cat 112 (4%)	—	Cat 112 (2%)	Cat 112 (4%)	—	Cat 112 (2%)	Cat 112 (4%)
Temperature, ° C	—	400	400	—	400	400	—	400	400
Initial H_2 pressure (cold), kg/cm²	—	100	100	—	100	100	—	100	100
Reaction pressure, kg/cm²	—	233	220	—	230	220	—	220	225
Reaction time, hr	—	3	3	—	3	3	—	3	3
Product obtained, %	—	87·5	92·0	—	90·5	87·5	—	91·0	87·0
Fraction up to 200° C, % on product	—	45·4	47·5	—	11·7	18·2	—	6·2	10·8
Fraction (200°–350° C), % of product	—	45·1	48·0	—	78·2	73·1	—	73·8	72·6
Residue and loss, %	—	9·5	4·5	—	10·1	8·7	—	20·0	16·6
Properties of oil boiling between 200°–350° C:									
Aniline point, ° C	25·6	45·4	54·0	26·8	46·4	54·6	37·2	39·0	44·6
Saturates, %	11·0	84·0	82·0	3·9	66·0	74·0	23·0	50·0	60·0
Unsaturates, %	17·5	—	2·0	12·0	4·0	2·0	24·0	6·0	4·0
Aromatics, %	71·5	16·0	16·0	84·0	30·0	24·0	52·0	44·0	36·0
Sp gr (60° F)	—	—	0·84	—	0·87	0·854	—	0·91	0·89
Diesel index	—	—	48·0	—	36·0	45·0	—	24·5	30·8

TABLE VI

Operating Variables and Characteristics of Products of Hydrogenation of Neutral Tar Oil (a) 200°–250° *C*, (b) 250°–300 *C*, (c) 300°–350° *C from Upper Kajora Tar—Effect of Temperature using Catalyst* 112

Samples hydrogenated	Upper Kajora neutral tar oil (200°–250° C)		Upper Kajora neutral tar oil (250°–300° C)		Upper Kajora neutral tar oil (300°–350° C)	
Experiment No.	H-137	H(c)-168	H-139	H(c)-170	H-141	H(c)-171
Catalyst	Cat 112 (4%)	Cat 112 (4%)	Cat 112 (4%)	Cat 112 (4%)	Cat 112 (4%)	Cat 112 (4%)
Temperature, ° C	400	425	400	425	400	425
Initial H_2 pressure, kg/cm² (cold)	100	100	100	100	100	100
Reaction pressure, kg/cm²	220	227	220	195	225	227
Reaction time, hr	3	3	3	3	3	3
Products obtained, %	92·0	77·0	87·5	79·0	87·0	85·0
Fraction up to 200° C, % of product	47·5	49·9	18·2	27·1	10·8	15·8
Fraction 200°–350° C, % on production	48·0	41·1	73·1	61·3	72·6	81·7
Residue and loss, %	4·5	9·0	8·7	11·6	16·6	2·5
Properties of oil boiling between 200°–350° C:						
Aniline point, °C	54·0	30·0	54·6	34·0	44·6	32·8
Saturates, %	82·0	46·0	74·0	48·0	60·0	48·0
Unsaturates, %	2·0	2·0	2·0	4·0	4·0	4·0
Aromatics, %	16·0	52·0	24·0	48·0	36·0	48·0
Sp gr (60° F)	0·84	—	0·854	—	0·89	—
Diesel index	48·0	—	45·0	—	30·8	—

and saturates, the aniline points of the samples were different. This may be attributed to the presence of relatively higher amounts of naphthenic components in the product of H-136, which contributed to the lowering of aniline point.

The properties of diesel oil fractions from 300°–350° C tar oils were generally poor, due to the relatively higher aromatic contents in this fraction. This confirmed the earlier experiments. However, it is evident from the results of these experiments that performance of catalyst 112 is superior to that of the other catalysts tested.

(4) *Effect of Temperature*

A few experiments were performed to explore the effect of temperature on the hydrogenation of these tar oil fractions, using catalyst 112. These results are tabulated in Table VI. With a 25° C increase in temperature, the yield and quality of diesel oil

fractions of the products deteriorated seriously for all the samples tested.

(5) *Hydrogenation of Low Temperature Neutral Tar Oil Fractions in a Bench Scale Continuous Reactor Using Complex Catalyst Containing Cobalt, Molybdenum, and Chromium at Low Pressure*

Studies on the hydrogenation of neutral low temperature tar oil fractions were continued in a continuous bench scale reactor (Fig 2). Some experiments were conducted on the effect of temperature and oil feed rate on hydrogenation of 200°–250° C neutral oil fraction using the above catalyst in a granulated form at a partial of H_2 of 50 kg/cm². These results are tabulated in Table VII.

TABLE VII

Operating Variables and Characteristics of Products of Hydrogenation of 200°–250° C Fraction Neutral Oil from Upper Kajora Low Temperature Tar—Effect of Temperature and Oil Rate Using Co–Mo–Cr *Catalyst*

Experiment No.	Analysis of feed-stock	No. 22	No. 23	No. 24
Catalyst	—	Co–Mo–Cr	Co–Mo–Cr	Co–Mo–Cr
Special velocity, vol oil/vol cat/hr	—	0·33	0·82	0·44
Temperature, ° C	—	400	500	500
Pressure, kg/cm²	—	50	50	50
Rate H_2 input cu ft/min (calculated from tail gas rate)	—	0·15	0·15	0·073
Ratio of gas to oil	—	3536	1600	1516
Product recovered, %	—	83·0	88·0	71·0
Boiling characteristics of product:				
Fraction up to 200° C, %	—	13·95	24·27	41·08
Fraction 200°–350° C, %	—	80·95	75·86	57·07
Residue and loss, %	—	5·05	1·87	1·85
Properties of 200°–350° C fraction:				
Sp gr (60° F)	0·876	0·87	0·868	0·886
Viscosity (Redwood 100° F), sec	30·26	30·6	30·3	Below 30·0
Flash point (Pensky–Martens closed), ° F	150·0	160·0	164·0	162·0
Aniline point, ° C	25·6	37·4	36·6	22·6
Conradson coke residue, %	0·047	0·051	0·089	0·042
Saturates, %	11·0	45·0	44·0	—
Unsaturates, %	17·5	4·0	4·0	—
Aromatics, %	71·5	51·0	52·0	—
Analysis of the 200°–350° C fraction:				
Carbon, %	85·9	87·28	87·56	88·96
Hydrogen, %	11·39	11·85	11·79	11·20
Sulphur, %	0·34	0·10	Traces	0·08
Nitrogen, %	0·04	0·09	0·14	0·12
Calorific value, Btu/lb	—	19,060	19,060	18,820
Diesel index	23·4	31·1	31·0	21·5

It is observed that on increasing the temperature from 400° to 500° C using a space velocity of about 0·4 (vol oil/vol cat/hr) the yield of diesel oil fraction drops from 80·95 to 57·07 per cent. The viscosity of the product at higher temperature falls below specification and the aniline point of the sample is found to be low. At 500° C and at increased space velocity of 0·82, substantial increase in the yield of diesel oil fraction was observed. The quality of the oil also compared favourably with products of lower temperature reaction and at lower space velocity. The effectiveness of catalyst 112 in the autoclave tests will be evident from Tables V and VI, and the results obtained using the granulated form of this catalyst in the continuous reactor are recorded in Table VIII.

TABLE VIII

Operating Variables and Characteristics of Products of Hydrogenation of 200°–250° C Fraction Neutral Tar Oil from Upper Kajora Low Temperature Tar—Effect of Temperature Using Catalyst 112

Experiment No.	Analysis of feed-stock	No. 25	No. 26
Catalyst	—	Cat 112	Cat 112
Space velocity, vol oil/vol cat/hr	—	0·48	0·48
Temperature, ° C	—	500	400
Pressure, kg/cm²	—	50	50
Product recovered, % by vol	—	84	78
Rate of H_2 input, cu ft/min (calculated from tail gas rate)	—	0·075	0·075
Ratio of H_2 to oil	—	1250	1250
Boiling characteristics of product:			
Fraction up to 200° C, %	—	47·2	16·17
Fraction 200°–350° C, %	—	47·7	82·26
Residue and loss, %	—	5·1	1·57
Properties of 200°–350° C fraction:			
Sp gr (60° F)	0·876	0·885	0·851
Viscosity (Redwood at 100° F), sec	30·26	30·0	30·4
Flash point (Pensky–Martens closed), ° F	150·0	152·0	164·0
Aniline point, ° C	25·6	Below 20	40·6
Conradson coke residue, %	0·047	0·073	0·092
Saturates in oil, %	11·0	30·0	47·0
Unsaturates in oil, %	17·5	4·0	4·0
Aromatics in oil, %	71·5	66·0	49·0
Analysis of 200°–350° C fraction:			
Carbon, %	85·9	89·04	81·17
Hydrogen, %	11·39	10·57	12·06
Sulphur, %	0·34	Traces	Traces
Nitrogen, %	0·04	Traces	Traces
Calorific value, Btu/lb	18,690	18,640	19,120
Diesel index	23·4	Below 20	36·5

(6) *Effect of Temperature on the Hydrogenation of 200°–250° C Neutral Tar Oil Fraction in a Bench Scale Continuous Reactor Using Catalyst* 112

These results indicate that on increasing the temperature from 400° to 500° C, yield of diesel oil fraction drops from 82 to 47 per cent. The specific gravity of the oil is also much lower at reaction temperature of 400° C, and a remarkable difference in aniline point of the products is observed. The quality of the product obtained at 400° C with this catalyst is much superior to that any of the other product obtained with Co–Mo–Cr catalyst, and this confirms the superiority of catalyst 112, as shown by earlier experiments done in batch autoclaves.

(7) *Hydrogenation of 250°–300° C Fraction of Neutral Tar Oil from Low Temperature Tar Using* Co–Mo–Cr *Catalyst in Bench Scale Continuous Reactor*

Results of these experiments are tabulated in Table IX. It is observed that increase of temperature from 400° to 500° C apparently does not produce any remarkable change in the characteristics of the diesel oil fraction. A somewhat higher yield of diesel oil was obtained at 500° C. The quality of the product was also inferior. On subjecting the diesel oil fraction from the run conducted at 400° C to rehydrogenation under identical conditions, no improvement in product was observed. The quality of the product is inferior to the 400° C hydrogenated product, as can be observed from the table.

TABLE IX

Operating Variables and Characteristics of Products of Hydrogenation of 250°–300° C Fraction Neutral Tar Oil from Upper Kajora Low Temperature Tar—Effect of Temperature Using Co–Mo–Cr *as Catalyst*

Particulars	Analysis of feedstock	No. 27	No. 28	No. 32
Catalyst	—	Co–Mo–Cr	Co–Mo–Cr	Co–Mo–Cr
Space velocity, vol oil/vol cat/hr	—	0·575	0·575	0·515
Temperature, ° C	—	400	500	400
Pressure, kg/cm²	—	50	50	50
Rate of H_2 input, cu ft/min (calculated from tail gas rate)	—	0·115	0·115	0·113
Ratio of H_2 to oil	—	1415	1415	1552
Product recovered, %	—	85·0	95·0	—
Boiling characteristics of product:				
Fraction up to 200° C, %	—	2·0	7·0	11–47
Fraction 200°–350° C, %	—	94·0	90·0	79·4
Residue and loss, %	—	4·0	3·0	8·9
Properties of 200°–350° C fraction:				
Sp gr (60° F)	0·934	0·903	0·907	—
Viscosity (Redwood at 100° F), sec	36·6	34·5	34·1	28·8
Flash point (Pensky–Martens closed), ° F	174·0	196·0	196·0	—
Aniline point, ° C	26·8	35·6	34·8	—
Conradson coke residue, %	0·092	0·051	0·043	—
Saturates in oil, %	12·0	34·5	34·0	30·0
Unsaturates, %	3·0	12·5	5·5	6·0
Aromatics, %	84·0	52·0	59·5	63·0
Analysis of 200°–350° C fraction:				
Carbon, %	87·76	88·01	88·71	—
Hydrogen, %	10·48	10·89	10·69	—
Nitrogen, %	Traces	Traces	Traces	—
Sulphur, %	Traces	Traces	Traces	—
Calorific value, Btu/lb	18,320	18,580	18,610	—
Diesel index	15·9	24·2	22·7	—

(8) *Hydrogenation of* 300°–350° *C Fraction of Neutral Tar Oil from Low Temperature Tar Using* Co–Mo–Cr *Catalyst in Bench Scale Continuous Reactor*

Results of these experiments are recorded in Table X. As in the previous case, no noticeable change in the characteristics of the product was obtained on changing the reaction temperature from 400° to 500° C. Yield and quality of product was somewhat better at the lower temperature. The product was characterized by high aromatic content and low aniline point. The other physical properties also suggested the unsuitability of this fraction for the production of diesel oil.

TABLE X

Operating Variables and Characteristics of Product of Hydrogenation of 300°–350° *C Fraction Neutral Oil from Upper Kajora Low Temperature Tar—Effect of Temperature using* Mo–Co–Cr *as Catalyst*

Experiment No.	Analysis of feedstock	No. 29	No. 30
Catalyst	—	Co–Mo–Cr	Co–Mo–Cr
Space velocity, vol oil/vol cat/hr	—	0·625	0·575
Temperature, ° C	—	400	500
Pressure, kg/cm²	—	50	50
Rate of H_2 in input, cu ft/min (calculated from tar gas rate)	—	0·112	0·116
Ratio of H_2 to oil	—	1267	1427
Product recovered, %	—	75·0	86·0
Boiling characteristics of product:			
Fraction up to 200° C, %	—	1·78	6·25
Fraction, 200°–350° C, %	—	80·56	74·05
Residue and loss, %	—	17·6	19·3
Properties of 200°–350° C fraction:			
Sp gr at 60° F	0·968	0·952	0·958
Viscosity (Redwood at 100° F), sec	47·8	39·6	38·4
Flash point (Pensky–Martens closed), ° F	142·0	204·0	212·0
Aniline point, ° C	37·2	30·8	27·0
Conradson coke residue, %	0·125	0·083	0·081
Saturates in oil, %	23·0	27·5	20·0
Unsaturates in oil, %	24·0	8·0	8·0
Aromatics in oil, %	52·0	63·5	70·0
Analysis of 200°–350° C fraction:			
Carbon, %	88·74	88·52	89·47
Hydrogen, %	9·30	9·85	9·44
Sulphur, %	0·39	Traces	Traces
Nitrogen, %	0·47	0·32	0·35
Calorific value, Btu/lb	17,860	18,240	18,090
Diesel index	14·6	14·64	12·9

CONCLUSION

Autoclave tests on the hydrogenation of untreated as well as treated fractions of low temperature tar from carbonization of a Raniganj coal indicate that both 200°–250° C and 250°–300° C fractions can be converted to diesel oils at 400° C and 200–267 mg/cm² partial pressure of hydrogen. Ni–Al catalyst appears to be particularly active when 250°–300° C tar fraction is used as feedstock at 400° C and 5-hour reaction period with 10 per cent catalyst concentration at a reaction pressure of 253·3 kg/cm².

Catalyst 112 gave uniformly better results than the other catalysts tested, and both 200°–250° C and 250°–300° C fractions could be processed to diesel oils, using 4 per cent of this catalyst at 226 kg/cm² partial pressure of hydrogen and at 400° C temperature and 3 hours reaction time.

Work in the continuous bench scale reactor shows that at low pressures (50 kg/cm²) the same tar oil fractions can be processed using Co–Mo–Cr and catalyst 112. When Co–Mo–Cr is used, the desired grade of product can be obtained at 500° C and at higher rates of oil feed. Catalyst 112 is, however, very sensitive to higher temperatures and the optimum temperature for the best reaction of this catalyst has been found to be 400° C for both 200°–250° C and 250°–300° C tar oil fractions.

The products of low pressure hydrogenation are somewhat inferior in quality to the products from high pressure reaction as obtained in autoclave tests. This low grade diesel can, however, be further processed to the desired grade of diesel oil by solvent extraction of aromatics partially or wholly, either before or after hydrogenation. The tar oil fraction 300°–350° C is, however, unsuitable for processing to high quality diesel oil, as shown both in autoclave and continuous plant tests, due to the refractory nature of the aromatics towards hydrogenolysis.

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MEASUREMENT OF GAS-PHASE SATURATION IN A POROUS MEDIUM *

By R. W. SNELL †

SUMMARY

The measurement of the gas-phase saturation in the laboratory study of the flow behaviour of three immiscible fluids in a porous medium is of paramount importance, especially to the oil producing industry. A neutron method is described and the results obtained show that the method is capable of indicating gas saturation to within ±2 per cent of the void volume.

In three-phase (oil, water, and gas) relative permeability/saturation measurements in a porous medium, the greatest difficulty has been experienced in determining the fraction of the pore space occupied by the gas phase. Most workers in this field have attempted to determine saturations under dynamic conditions rather than measurements made on samples of the medium after flow has ceased.

Determination of water-phase saturation is usually made by conductivity measurements between electrodes in the flow cell,[1, 2] or by induced electrical phenomena [3–5] and is relatively simple.

Saturation to the oil phase has been measured by X-ray [6, 7] and gamma-ray absorption,[8] radioactive tracer methods,[9, 10] and by a neutron method.[11]

The absorption methods suffer from the complication that both oil and water absorb the radiations to different degrees and in order to determine the third (gas) phase saturation, by subtraction, a knowledge of the saturation of one of the other phases is required in order to use the absorption curves, which must be plotted as functions of both oil and water saturations.

The handling of bulk radioactive tracer fluids can be fraught with danger and is not very convenient in ordinary laboratories.

In the method here described the effect of both oil and water is identical (within the experimental limits), and it is possible to obtain a direct plot of gas saturation against thermal neutron count without stopping flow and there is no radiation shielding problem.

When fast neutrons collide with heavy nuclei they are deflected with little loss in energy, but when the collision occurs with a nucleus of comparable mass the neutron is slowed down to what is termed " thermal " energy. The relative energy lost by the neutron in a collision with another nucleus is determined by the angle at which it happened to scatter and by the mass of the struck nucleus.

The minimum energy the neutron can have after a collision is when the neutron is deflected through 180°, and it can be shown that, excepting hydrogen, the neutron must retain at least 72 per cent of its original energy. (This lower limit holds for a collision with the carbon nucleus.) On the average, energy losses amount to one-half the calculated maximum. In the case of a collision with the hydrogen nucleus, the neutron can lose all its energy in a head-on collision, but this is comparatively rare, and it may be shown that the energy range of the scattered neutron is between zero and its original energy. The average energy after scattering by hydrogen is one-half of the original neutron energy. Neutrons in this range of energy are termed " thermal " neutrons and are easily detected by a boron trifluoride proportional counter.

The method has been adequately described in the literature [12–14] and has become a useful tool in the soil mechanics field for determination of moisture content in shallow boreholes and on the surface.

The oil well electric logging companies also use neutron methods for oil well surveying, but have, as yet, measured only the induced gamma radiation from the capture of the thermal neutrons by the heavier nuclei.

A neutron method was first used in this field by Brunner and Mardock [11] in 1945, but at that time the BF_3 counter did not exist. The thermal neutrons produced by the oil phase on fast neutron bombardment were detected by the gamma radiation they induced in a rhodium plate placed in contact with the flow cell. The plate was removed and after a fixed time its radioactivity was measured with a standard G–M tube.

The apparatus used to detect thermal neutrons is shown schematically in Fig 1. The neutrons were derived from a 500 mc Po–Be source which was mounted beside the counter tube. The counter itself was mounted on a trolley which enabled the system to scan the experimental flow tube and two reference cells.

The flow tube itself consisted of a 4-inch od perspex tube filled with 80–100 mesh BSS silver sand packed to a porosity of 35 per cent. The two reference cells were similarly packed, one being 100 per cent water saturated and the other 100 per cent gas

* MS received 19 January 1959.

† Chemical Engineering Dept, The University, Birmingham.

saturated, and were used for frequent calibration of the counting system owing to the fairly rapid decline of the neutron source. (Polonium half-life 136 days.)

The counting rate for the system in the early life of the polonium source was from 1600 counts/minute for the 100 per cent water-saturated reference cell to

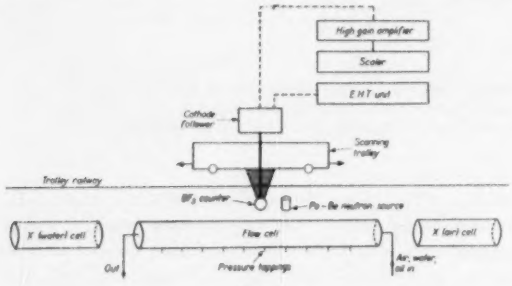

FIG 1

700 counts/minute for the 100 per cent air-saturated reference cell and the normal counting time was 10 minutes each for the three counts required to determine the saturation/relative thermal neutron count relationship.

TABLE I

Fluid Saturation State and Relative Neutron Counts

Air	Saturation % water	Oil	% Relative neutron count
0	0	100	101·0 *
0	100	0	100·0 †
0	100	0	100·1 ‡
0	77·8	22·2	99·1
0	72·4	27·6	100·0
0	55·8	44·2	100·2
0	34·5	65·5	96·8
0	20·9	79·1	100·1
3·0	76·8	20·2	86·0
3·0	76·8	20·2	88·2
6·8	60·0	33·2	79·0
14·3	64·4	21·3	64·0
16·8	50·0	33·2	58·2
24·0	54·8	21·2	43·2
26·8	40·0	33·2	42·2
35·0	44·0	21·0	32·2
35·0	44·0	21·0	31·5
38·9	31·0	30·1	23·7
39·2	27·6	33·2	23·5
39·5	35·0	25·5	24·0
45·0	34·2	20·8	20·1
49·5	29·8	20·7	18·7
50·0	22·7	27·3	19·2
52·7	26·7	20·6	16·2
55·7	18·8	25·5	12·3
55·7	18·8	25·5	13·8
100	0	0	0 §

* Oil-saturated reference cell.
† Water-saturated reference cell.
‡ Water-saturated main cell, initial condition.
§ Air-saturated reference cell.

Various three-phase static saturations were obtained and the relative thermal neutron intensities were recorded (see Table I).

It was found that the response to the oil phase and to the water was similar, within the experimental limits, and the presentation of results could be made as a plot of relative neutron count against gas saturation.

The oil in the experiment was a mixture of gas oil and lubricating oil of viscosity about 10 cP at room temperature and the water contained 5 g/litre of NaCl.

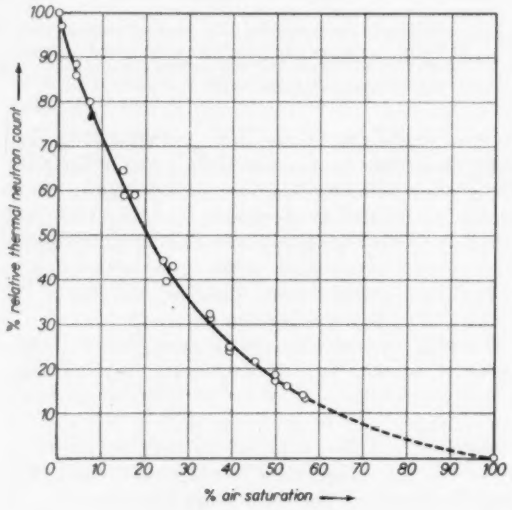

FIG 2

THERMAL NEUTRON COUNT *v.* AIR SATURATION

Obtained on an unconsolidated silver sand of 6 darcies permeability and 35 per cent porosity

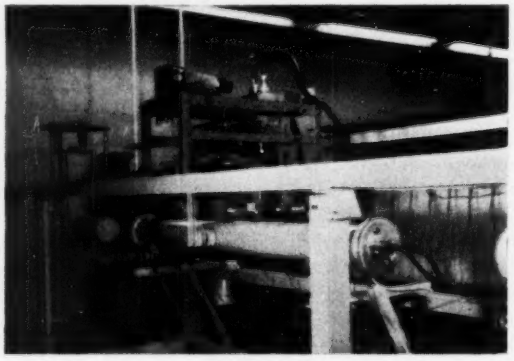

FIG 3

GENERAL VIEW OF REAR OF APPARATUS

Showing BF_3 counter, source holder, main flow cell, and reference cell

With a high salt content, because of the high " cross-section " of sodium and chlorine, considerable thermal neutron capture would have taken place with a consequent induced gamma radiation and a

difference in thermal neutron density between the oil and water phases. Thus the hydrogen densities of the chosen fluids were in close agreement. The gas phase used was air in these experiments, but the method is equally applicable to all gases at low pressures.

From measurements made on two sand packs the gas saturation could be determined to within ± 2 per cent.

The hydrogen content of the perspex cell appeared as a " background " thermal neutron count and cancelled out in the relative neutron density expression.

A typical curve of relative neutron density v. percentage of air saturation is shown in Fig 2.

$$\text{Relative neutron density} = \frac{X_{(\text{sat})} - X_{(\text{air})}}{X_{(\text{water})} - X_{(\text{air})}} \quad 100$$

per cent where

$X_{(\text{sat})}$ = neutron count at particular saturation.
$X_{(\text{air})}$ = neutron count at 100 per cent air saturation.
$X_{(\text{water})}$ = neutron count at 100 per cent water saturation.

ACKNOWLEDGMENTS

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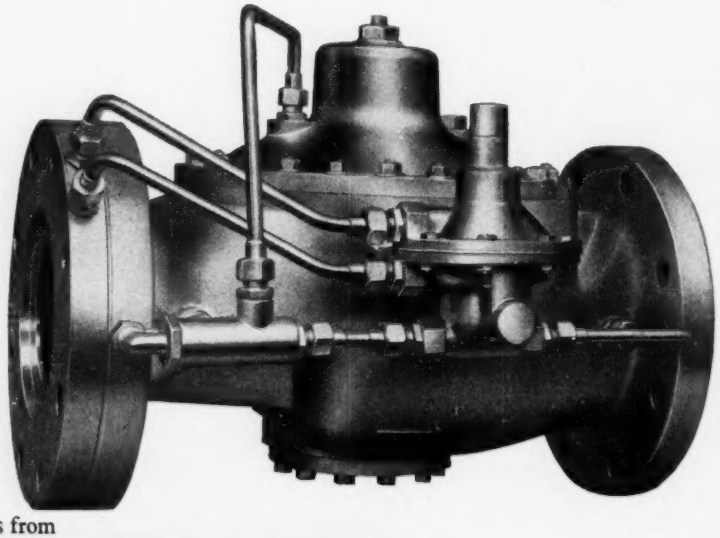

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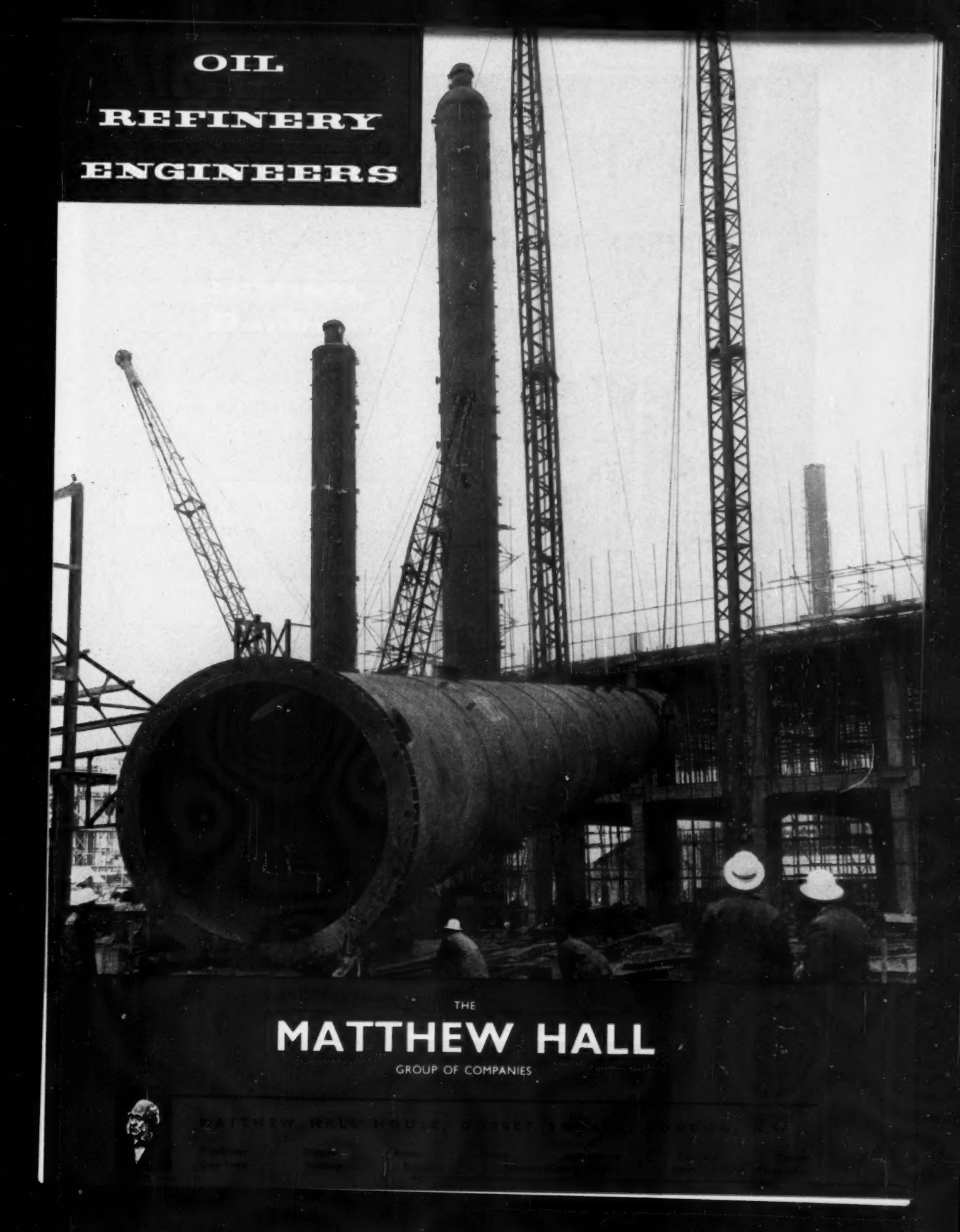

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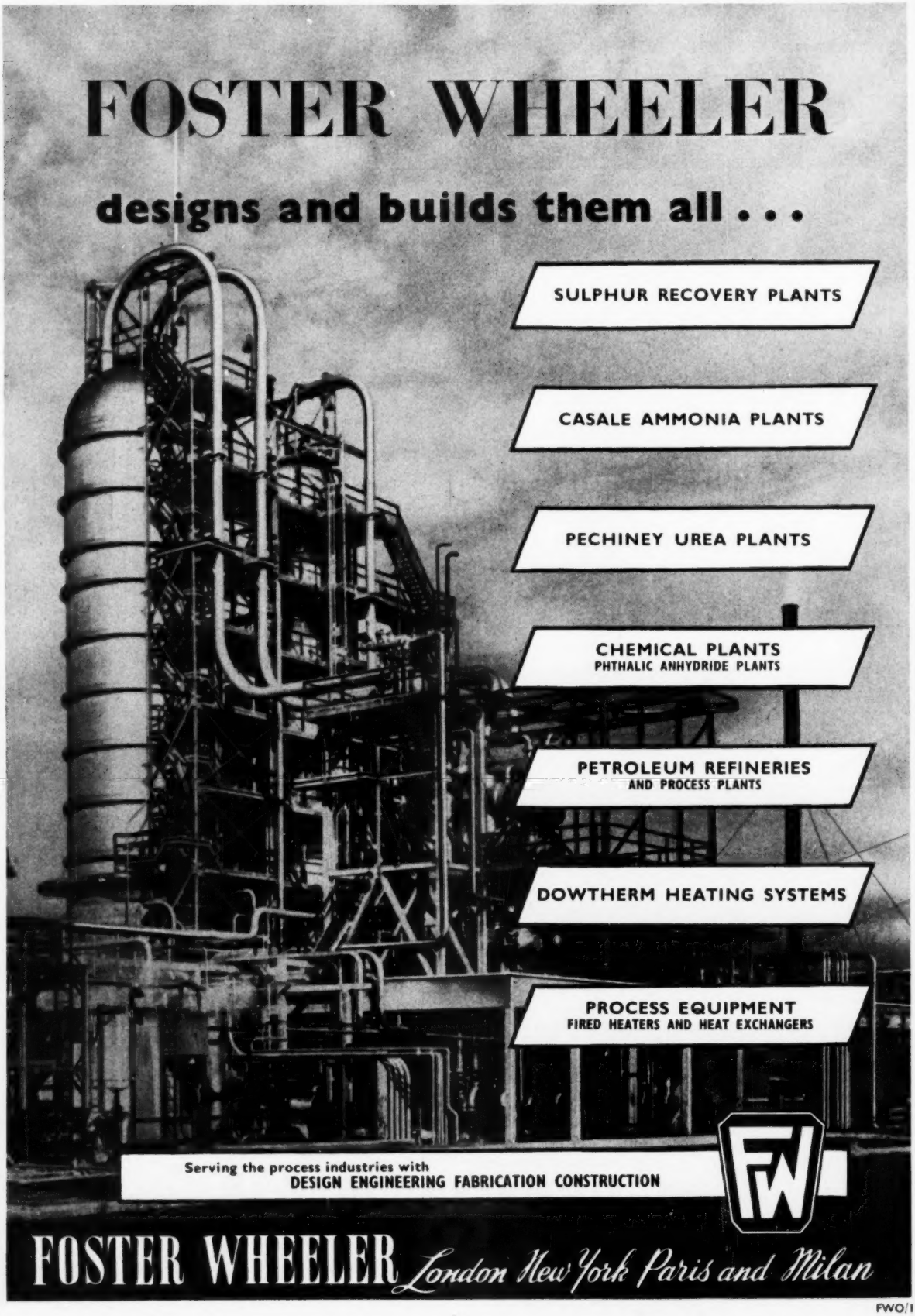
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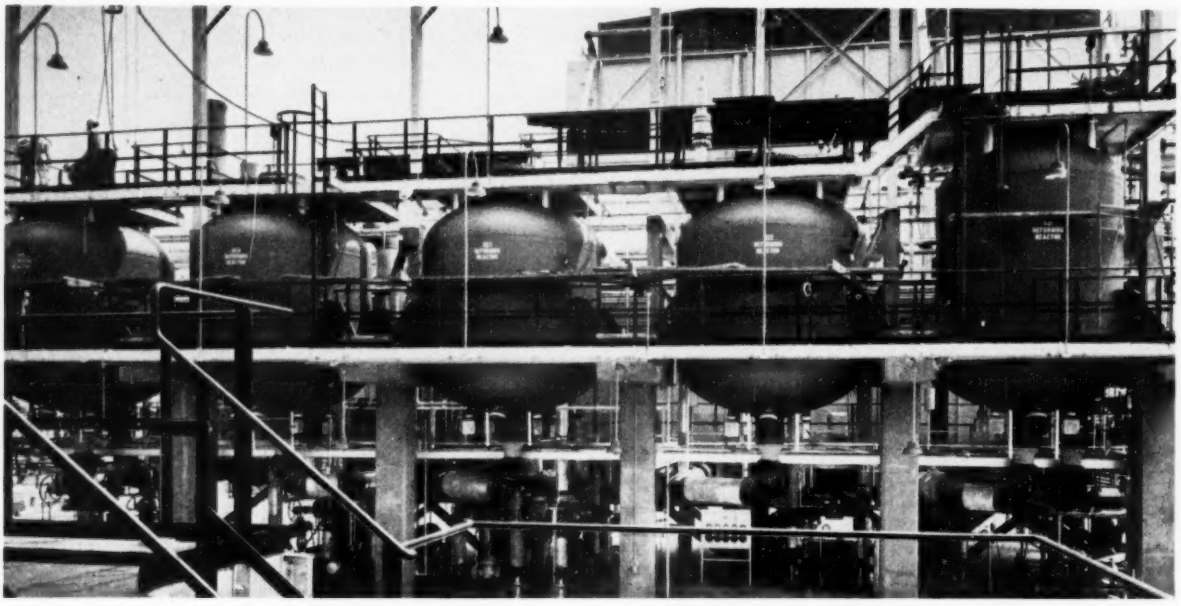

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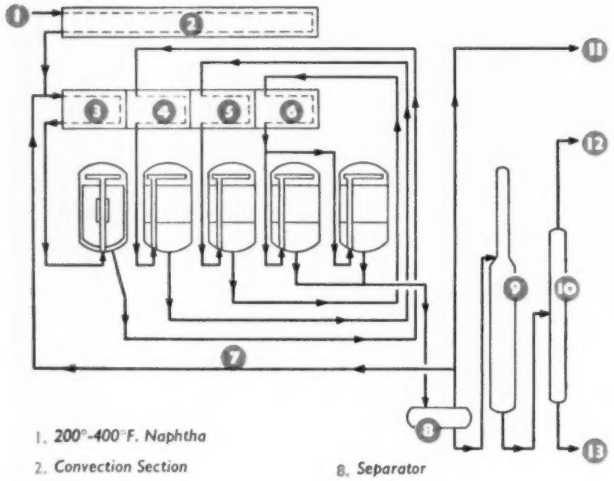

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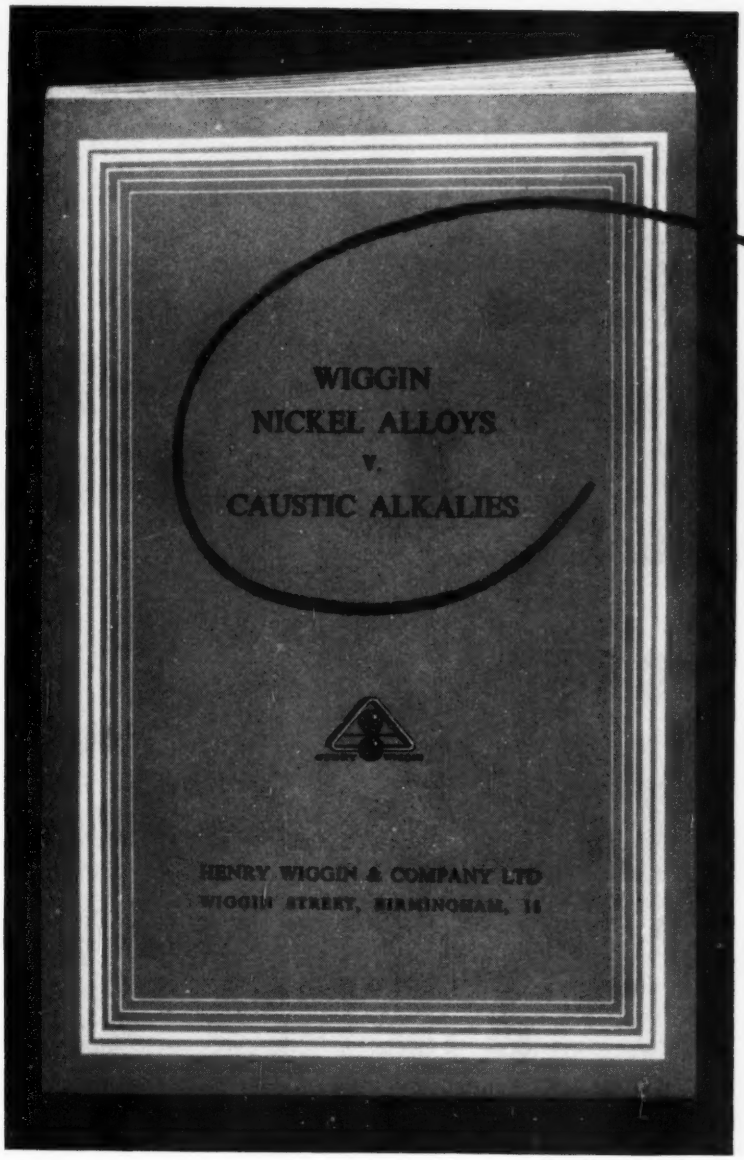

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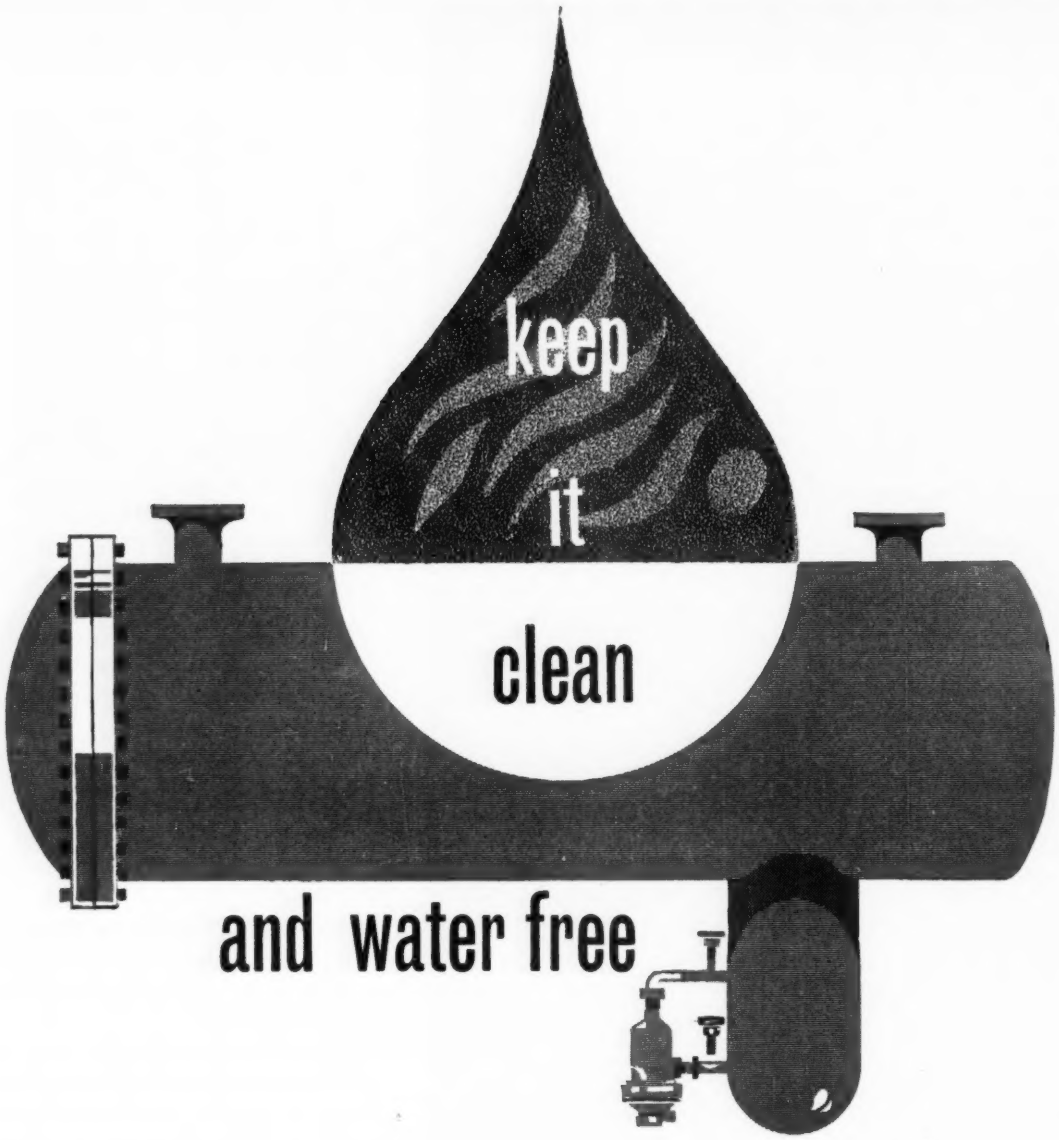

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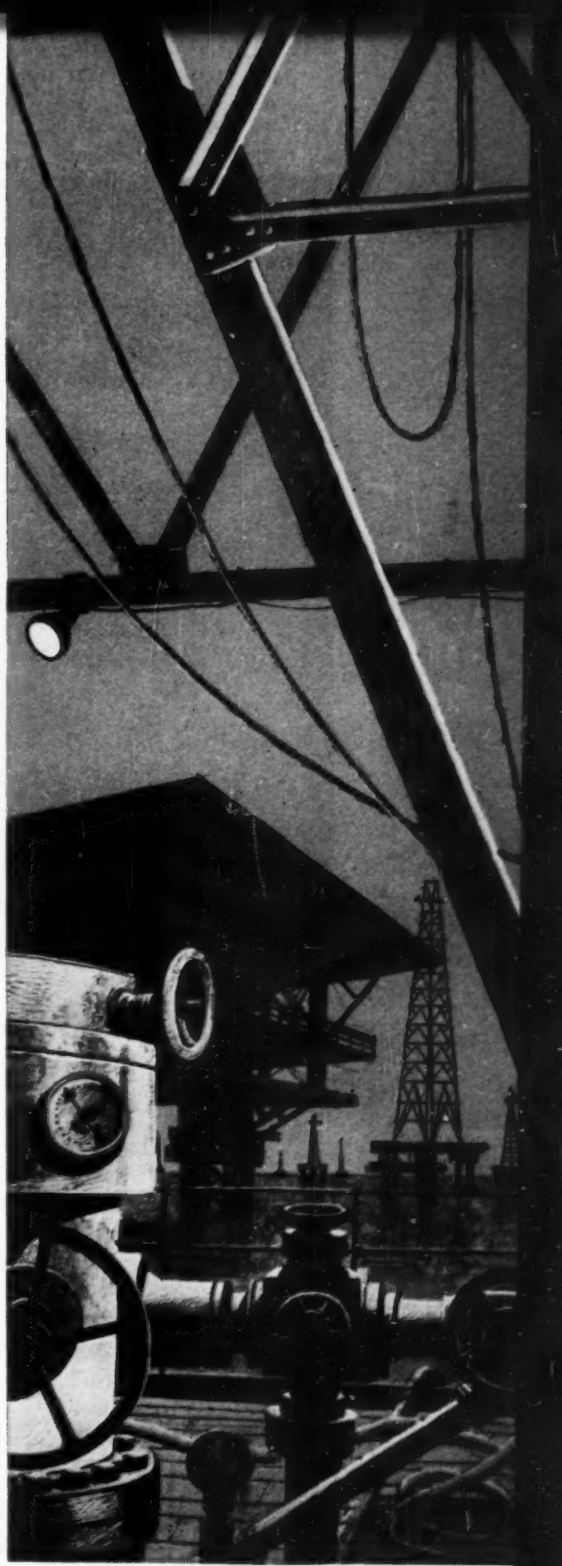

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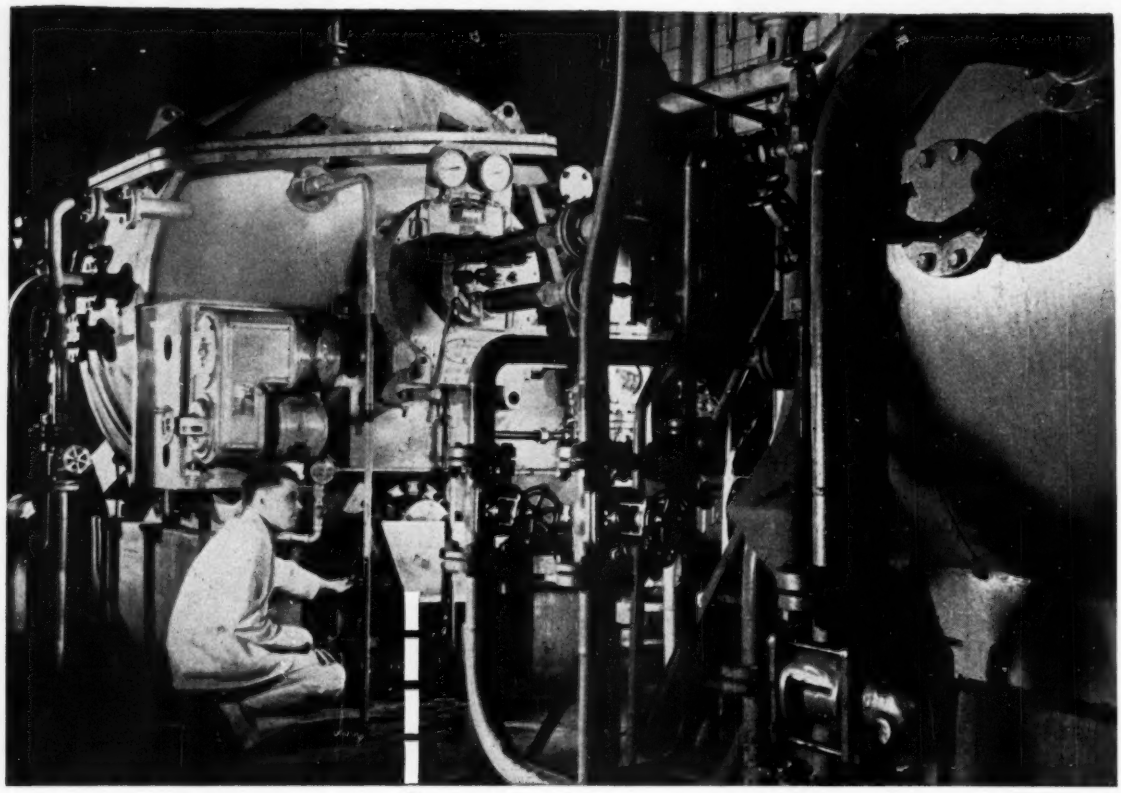

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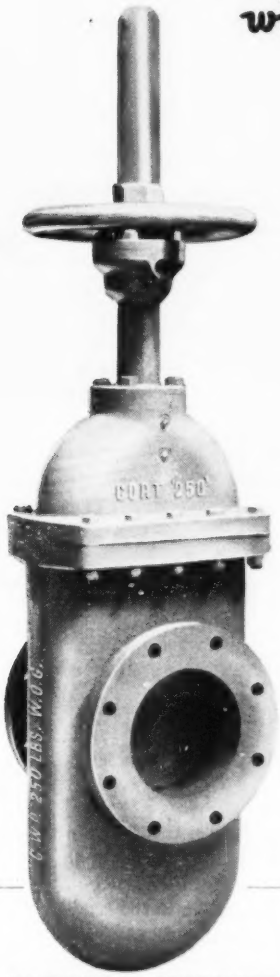

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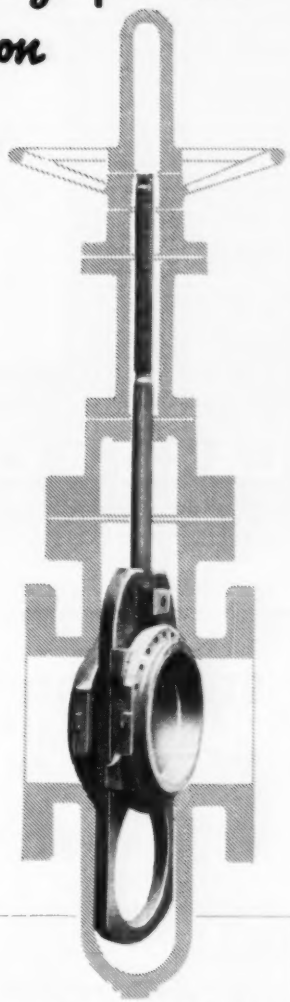

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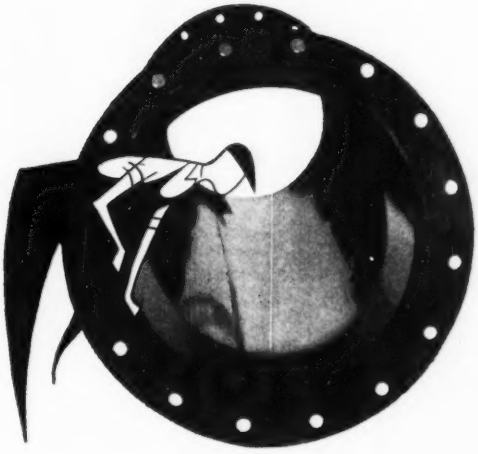

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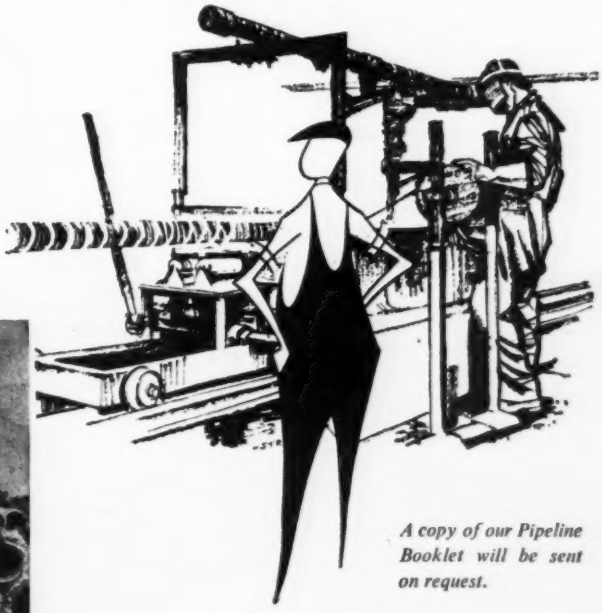

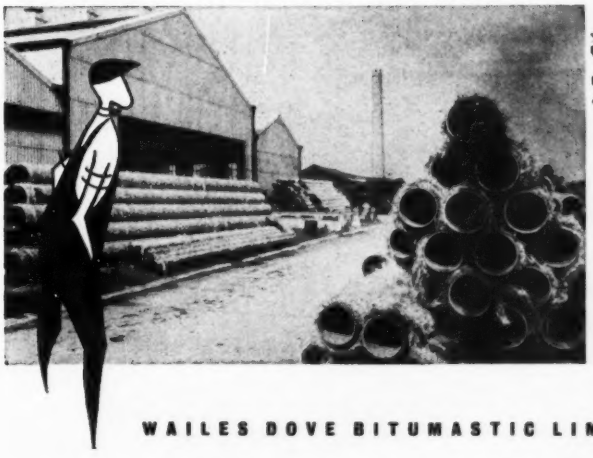

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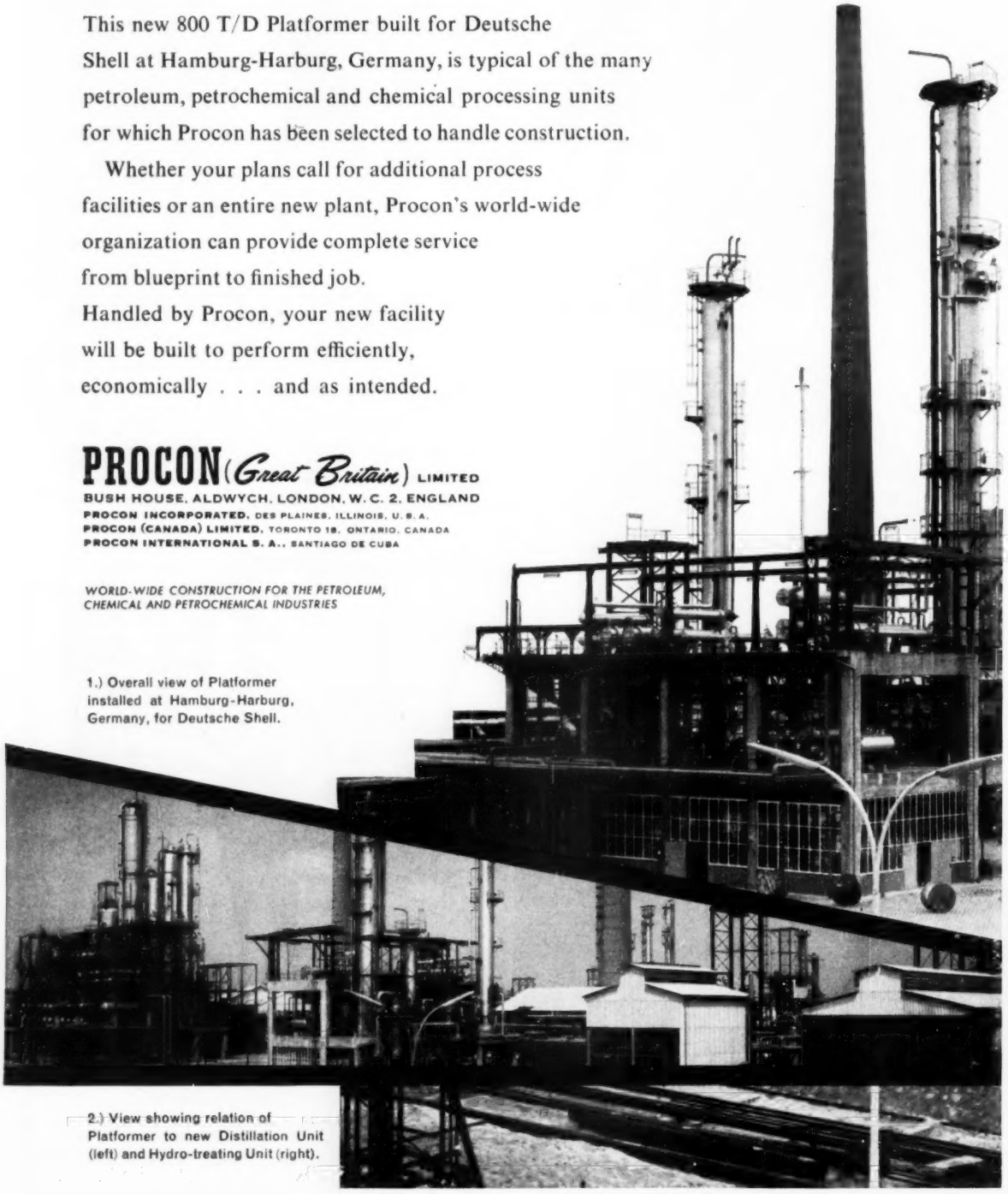

1.) Overall view of Platformer installed at Hamburg-Harburg, Germany, for Deutsche Shell.

2.) View showing relation of Platformer to new Distillation Unit (left) and Hydro-treating Unit (right).

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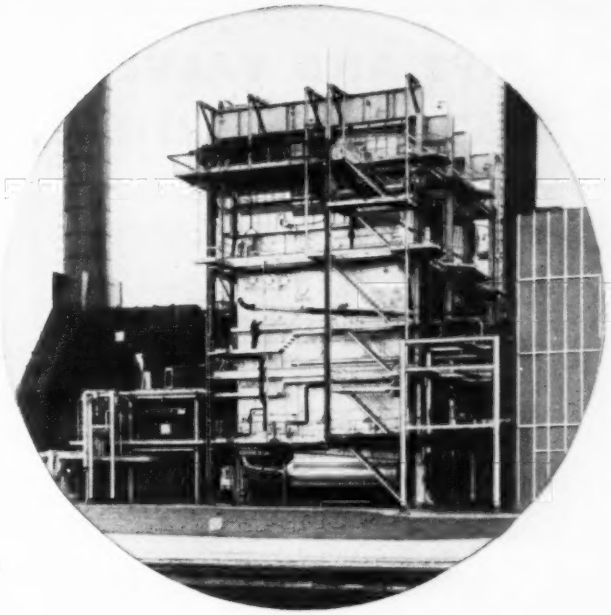

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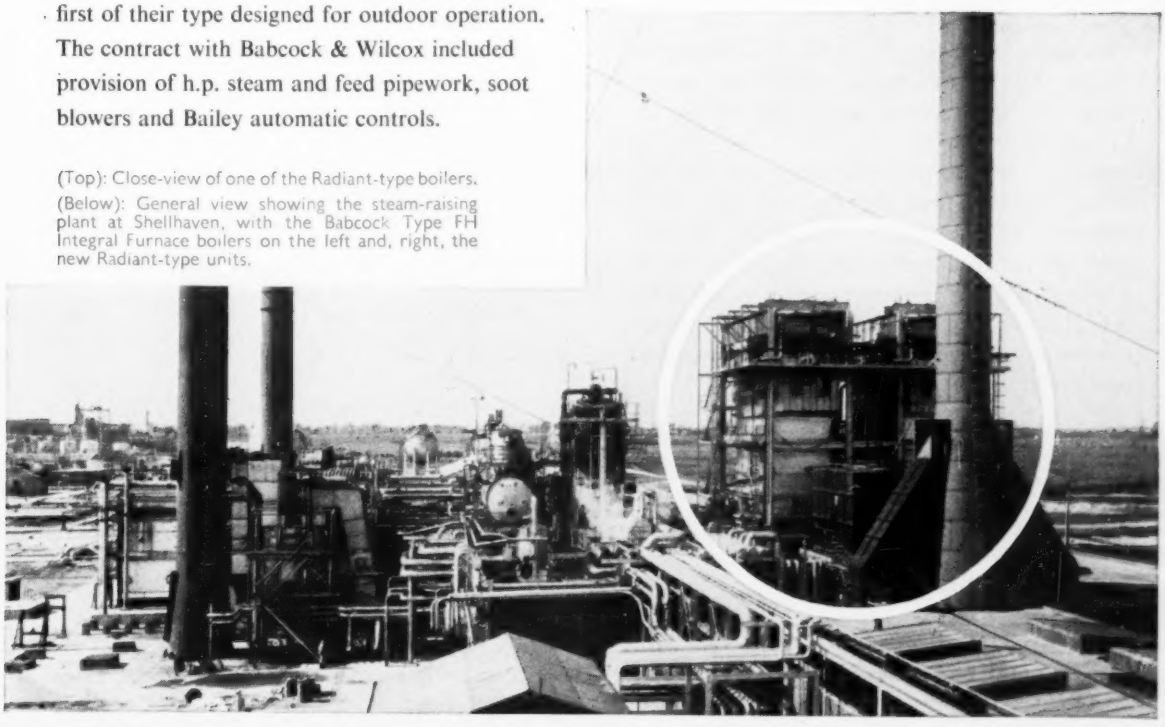
(Top): Close-view of one of the Radiant-type boilers.
(Below): General view showing the steam-raising plant at Shellhaven, with the Babcock Type FH Integral Furnace boilers on the left and, right, the new Radiant-type units.



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